



STATEMENT

I, Noashi KATAMURA—of ARK Mori Building, 13F, 12-32, Akasaka 1-chome, Minato-ku, Tokyo 107-6013 Japan—hereby declare that I am conversant in both Japanese and English and that I believe the following is true and correct translation of Japanese Patent Application No. 2000-292537.

Date: June 18, 2004

N. Kitamura

Noashi KITAMURA



[Name of Document] Specification

[Title of the Invention] POSITIVE RESIST COMPOSITION

[Scope of Claims for a Patent]

[Claim 1] A positive resist composition comprising:

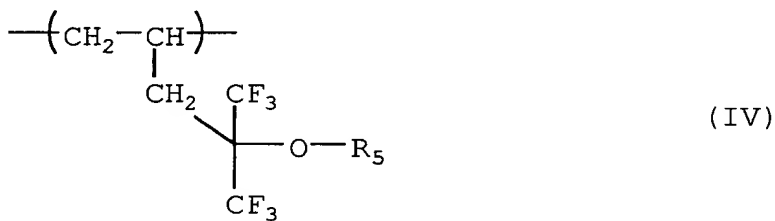
(A) a fluorine group-containing resin having: a structure wherein at least one of the main chain and the side chain of the polymer skeleton has at least one fluorine atom; and a group capable of decomposing under the action of an acid to increase the solubility in an alkali developer;

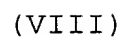
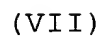
(B) a compound capable of generating an acid upon irradiation with one of an actinic ray and radiation; and

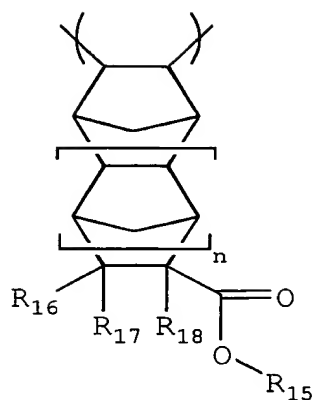
(C) a surfactant containing at least one of a silicon atom and fluorine atom.

[Claim 2] The positive resist composition as claimed in claim 1, wherein the resin (A) comprises one of a fluorine group-containing resin having at least one selected from a perfluoroalkylene group and a perfluoroarylene group, as a part or all of the main chain of the polymer skeleton; and a fluorine group-containing resin having at least one selected from a perfluoroalkyl group, a perfluoroaryl group, a hexafluoro-2-propanol group and a group wherein the OH group in a hexafluoro-2-propanol group is protected, as a part or all of the side chain of the polymer skeleton.

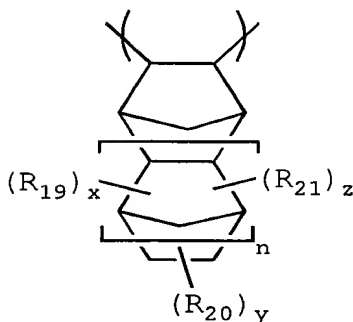
[Claim 3] The positive resist composition as claimed in claim 1 or 2 , wherein the resin (A) comprising one of a resin containing at least one of repeating units represented by formulae (I) to (III); a resin containing at least one of repeating units represented by formulae (IV) to (VII); or a resin containing at least one of repeating units represented by formulae (VIII) to (X):







(IX)



(X)

wherein R₀ and R₁ each represents a hydrogen atom, a fluorine atom, or an alkyl, perfluoroalkyl, cycloalkyl or aryl group, each of which may have a substituent;

R₂ to R₄ each represents an alkyl, perfluoroalkyl, cycloalkyl or aryl group, each of which may have a substituent and R₀ and R₁ may combine to form a ring, R₀ and R₂ may combine to form a ring and R₃ and R₄ may combine to form a ring;

R₅ represents a hydrogen atom, an alkyl, perfluoroalkyl, monocyclic or polycyclic cycloalkyl, acyl or alkoxycarbonyl group, each of which may have a substituent;

R₆, R₇ and R₈, which may be the same or different, each represents a hydrogen atom, a halogen atom or an alkyl,

perfluoroalkyl or alkoxy group, each of which may have a substituent;

R₉ and R₁₀, which may be the same or different, each represents a hydrogen atom, a halogen atom, a cyano group, or an alkyl or haloalkyl group, each of which may have a substituent;

R₁₁ and R₁₂, which may be the same or different, each represents a hydrogen atom, a hydroxyl group, a halogen atom, a cyano group, an alkoxy group, an acyl group, or an alkyl, cycloalkyl, alkenyl, aralkyl or aryl group, and the alkyl, the cycloalkyl, the alkenyl, the aralkyl or the aryl group each may have a substituent;

R₁₃ and R₁₄, which may be the same or different, each represents a hydrogen atom, a halogen atom, a cyano group, or an alkyl or haloalkyl, each of which may have a substituent;

R₁₅ represents an alkyl, monocyclic or polycyclic cycloalkyl, alkenyl, aralkyl or aryl group, each of which has a fluorine atom;

R₁₆, R₁₇ and R₁₈, which may be the same or different, each represents a hydrogen atom, a halogen atom, a cyano group, or an alkyl, perfluoroalkyl, alkoxy or -CO-O-R₁₅ group, each of which may have a substituent;

R₁₉, R₂₀ and R₂₁, which may be the same or different, each represents a hydrogen atom, a fluorine atom or an

alkyl, monocyclic or polycyclic cycloalkyl, alkenyl, aralkyl, aryl or alkoxy group, each of which has a fluorine atom, provided that at least one of R_{19} , R_{20} and R_{21} is a group other than a hydrogen atom;

A_1 and A_2 each represents a single bond, a divalent alkylene, alkenylene, cycloalkylene, arylene group, $-O-CO-R_{22}-$, $-CO-O-R_{23}-$ or $-CO-N(R_{24})-R_{25}-$, and the divalent alkylene, alkenylene, cycloalkylene or arylene group each may have a substituent;

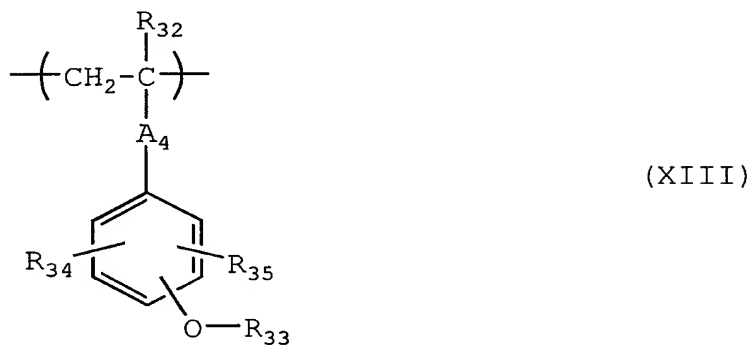
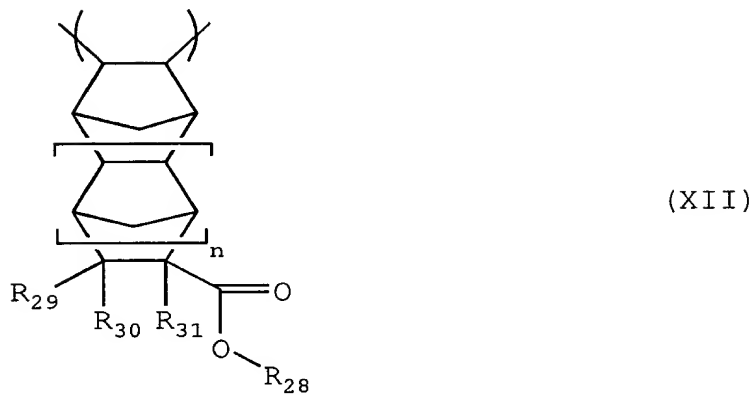
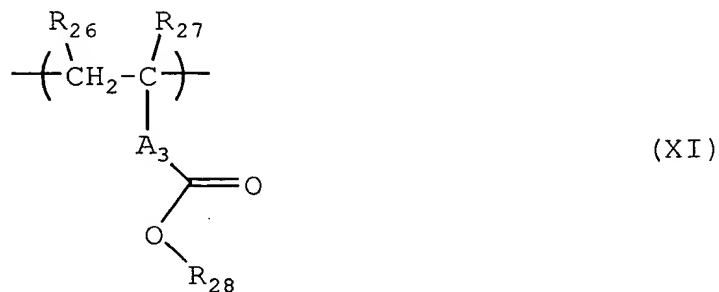
R_{22} , R_{23} and R_{25} , which may be the same or different, each represents a single bond or a divalent alkylene, alkenylene, cycloalkylene or arylene group, each of which may have an ether group, an ester group, an amide group, a urethane group or a ureido group;

R_{24} represents a hydrogen atom or an alkyl, cycloalkyl, aralkyl or aryl group, each of which may have a substituent;

n represents 0 or 1; and

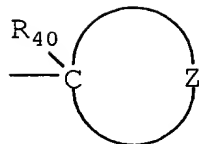
x , y and z each represents an integer of 0 to 4.

[Claim 4] The positive resist composition as claimed in any one of claims 1 to 3, wherein the resin (A) contains at least one of repeating units represented by formulae (XI) to (XIII):



wherein R_{26} , R_{27} and R_{32} , which may be the same or different, each represents a hydrogen atom, a halogen atom, a cyano group, or an alkyl or haloalkyl group, each of which may have a substituent;

R_{28} and R_{33} each represents $-\text{C}(\text{R}_{36})(\text{R}_{37})(\text{R}_{38})$, $-\text{C}(\text{R}_{36})(\text{R}_{37})(\text{OR}_{39})$ or a group represented by formula (XIV):



(XIV)

wherein R₂₉, R₃₀ and R₃₁, which may be the same or different, each represents a hydrogen atom, a halogen atom, a cyano group or an alkyl, perfluoroalkyl, alkoxy or -CO-O-R₂₈ group, each of which may have a substituent;

R₃₄ and R₃₅, which may be the same or different, each represents a hydrogen atom, a hydroxyl group, a halogen atom, a cyano group, an alkoxy group, an acyl group, or an alkyl, cycloalkylene, alkenyl, aralkyl or aryl group, and the alkyl, cycloalkylene, alkenyl, aralkyl or aryl group each may have a substituent;

R₃₆, R₃₇, R₃₈ and R₃₉, which may be the same or different, each represents an alkyl, cycloalkyl, alkenyl, aralkyl or aryl group, each of which may have a substituent, and two of R₃₆, R₃₇ and R₃₈, or two of R₃₆, R₃₇ and R₃₉ may combine to form a ring;

R₄₀ represents an alkyl, cycloalkyl, alkenyl, alkynyl, aralkyl or aryl group, each of which may have a substituent;

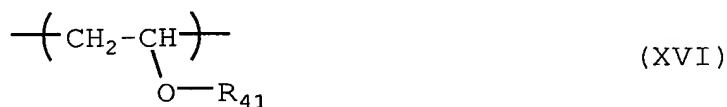
A₃ and A₄ each represents a single bond, a divalent alkylene, alkenylene, cycloalkylene, arylene group, -O-CO-R₂₂-, -CO-O-R₂₃- or -CO-N(R₂₄)-R₂₅-, and the divalent alkylene, alkenylene, cycloalkylene or arylene group each may have a substituent;

R₂₂ to R₂₅ have the same meanings as above;

Z represents an atomic group constituting a monocyclic or polycyclic alicyclic group together with the carbon atom; and

n represents 0 or 1.

[Claim 5] The positive composition as claimed in any one of claims 1 to 4, wherein the resin (A) contains at least one of repeating units represented by formulae (XV) and (XVI):



wherein R₄₁ represents an alkyl, cycloalkyl, aralkyl or aryl group, each of which may have a substituent.

[Claim 6] The positive resist composition as claimed in any one of claims 1 to 5, which further comprises a compound (D) containing a basic nitrogen atom as an acid diffusion inhibitor.

[Claim 7] The positive resist composition as claimed in any one of claims 1 to 6, wherein the compound (B) comprises at least one compound selected from sulfonium salt compounds

and iodonium salt compounds capable of generating, upon irradiation with one of an actinic ray and radiation, at least one of a perfluoroalkylsulfonic acid having 2 or more carbon atoms; a perfluoroarylsulfonic acid; and an arylsulfonic acid having a perfluoroalkyl group as a substituent.

[Claim 8] The positive resist composition as claimed in any one of claims 1 to 7, which is a composition to be irradiated with an ultraviolet ray having a wave length of 160 nm or less.

[Detailed Description of the Invention]

[Technical Field to Which the Invention Belongs]

The present invention relate to a positive resist composition suitable for use in the microlithography process in the production of VLSI or high-capacity microchip, or in other photo-fabrication processes. More specifically, the present invention relates to a positive resist composition capable of forming a highly definite pattern using a vacuum ultraviolet ray of 160 nm or less.

[Background Art]

The integration degree of integrated circuits is more and more intensified and in the production of a

semiconductor substrate of VLSI, an ultrafine pattern comprising lines having a width of quarter-micron or less must be processed. For achieving refinement of a pattern, means of using an exposure light source having a shorter wavelength in the formation of a resist pattern is known. This fact is supported by Rayleigh's formula:

$$R = k \cdot \lambda / NA$$

(wherein λ is a wavelength of the exposure light source, NA is a numerical aperture for a lens, k is a process constant), the formula representing the resolution (line width) R of the optical system. From this formula, it is understood that the wavelength λ of the exposure light source need to be shorten for achieving a high resolution, i.e., reducing the R value.

For example, in the production of a semiconductor device having an integration degree of up to 64 M bits, the i-line (365 nm) of a high-pressure mercury lamp has been heretofore used as the light source until today. For the positive resist respondent to this light source, a large number of compositions comprising a novolak resin and a naphthoquinone diazide compound as a photosensitive material have been developed and succeeded in giving a satisfactory result in the processing of lines having a width of about 0.3 μm or more. In the production of a semiconductor device having an integration degree of 256 M-

bits or more, a KrF excimer laser ray (248 nm) is employed as the exposure light source in place of the i-line.

Recently, for producing a semiconductor having an integration degree of 1 G-bit or more, an ArF excimer laser ray (193 nm) which is a light source having a short wavelength is used. Furthermore, use of an F₂ excimer laser ray (157 nm) is being studied for forming a pattern of 0.1 μm or less.

To cope with this tendency toward shorter wavelength of the light source, the resist material is greatly changed in its constituent components and chemical structure. More specifically, conventional resists comprising a novolak resin and a naphthoquinonediazide compound have large absorption in the far ultraviolet region at 248 nm and therefore, the ray may fail in reaching the resist bottom to a sufficient depth, as a result, only a tapered pattern and low sensitivity is obtained.

In order to solve this problem, a so-called chemical amplification-type resist, that is, a composition mainly comprising a resin having a basic skeleton of poly(hydroxystyrene) which shows small absorption in the region of 248 nm and is protected with an acid-decomposable group, and using in combination a compound (photoacid generator) capable of generating an acid upon irradiation with a far ultraviolet ray has been developed. In the chemical

amplification-type resist, the acid generated in the exposed area causes a catalytic decomposition reaction and thereby changes the solubility in a developer, so that a high-sensitivity and high-resolution pattern can be formed.

Acid decomposable resins and photoacid generators, effective for the chemical amplification-type resist, are reported in many papers, patent documents, such as Polym. Eng. Sci., vol. 23, page 1012 (1983), ACS. Sym., vol. 242, page 11 (1984), Macromolecules, vol. 21, page 1475 (1988), Journal of Synthetic Organic Chemistry, Japan, vol. 49, page 437 (1991), and "Fine Processing and Resist" (Kyoritsu Shuppan Co., Ltd., 1987).

However, the compound having an aromatic group originally has large absorption in the region at a wavelength of 193 nm and therefore, when an ArF excimer laser ray (193 nm) is used, even the above-described chemical amplification-type resist cannot provide sufficiently high performance.

To solve this problem, the acid decomposable resin having a basic skeleton of poly(hydroxystyrene) is replaced by an acid decomposable resin having incorporated into the main or side chain of the polymer an alicyclic structure having no absorption at 193 nm, with an attempt to improve the chemical amplification-type resist. Alicyclic acid decomposable resins are described in specifications in such

as JP-A-4-39665 (the term "JP-A" as used herein means an "unexamined published Japanese patent application"), JP-A-7-234511, JP-A-9-73173, JP-A-7-199467, JP-A-8-259656, JP-A-9-221519, JP-A-10-10739, JP-A-9-230595, JP-A-10-111569, JP-A-10-218947, JP-A-10-15386 and WO-97/33198.

However, this alicyclic resin has large absorption in the region of 157 nm and therefore, with use of an F₂ excimer laser ray (157 nm), is still deficient in obtaining an objective pattern of 0.1 μ m or less. On the other hand, Proc. SPIE., Vol. 3678, page 13 (1999) has reported that a resin having incorporated therein a fluorine atom (perfluoro-structure) has sufficiently high transparency to light at 157 nm, and effective fluorine resin structures have been reported in Proc. SPIE., Vol. 3999, page 330 (2000), ibidem., page 357 (2000), ibidem., page 365 (2000) and WO-00/17712.

The resists comprising such a fluorine resin are, however, not always satisfied with respect to the dry etching resistance and since these resins show peculiar water repellency or oil repellency attributable to the perfluoro-structure, improvement of the coatability (uniformity of the coated surface) and prevention of development defects are being demanded.

[Problems that the Invention is to Solve]

Accordingly, an object of the present invention is to provide a positive resist composition suitable for the case using an exposure light source of 160 nm or less, particularly a F₂ excimer laser ray (157 nm). More specifically, the object of the present invention is to provide a positive resist composition capable of exhibiting sufficiently high transparency on use of a light source at 157 nm and satisfying the properties with respect to the coatability and the development defect.

Another object of the present invention is to provide a positive resist composition capable of forming a pattern with good sensitivity and high resolution and ensuring excellent dry etching resistance.

[Means for Solving the Problems]

As a result of extensive investigations by taking account of various properties described above, the present inventors have found that the objects of the present invention can be successfully attained by the use of the following specific composition. The present invention has been accomplished based on this finding.

More specifically, the present invention has the following constructions.

(1) A positive resist composition comprising:

(A) a fluorine group-containing resin having: a

structure wherein at least one of the main chain and the side chain of the polymer skeleton has at least one fluorine atom; and a group capable of decomposing under the action of an acid to increase the solubility in an alkali developer;

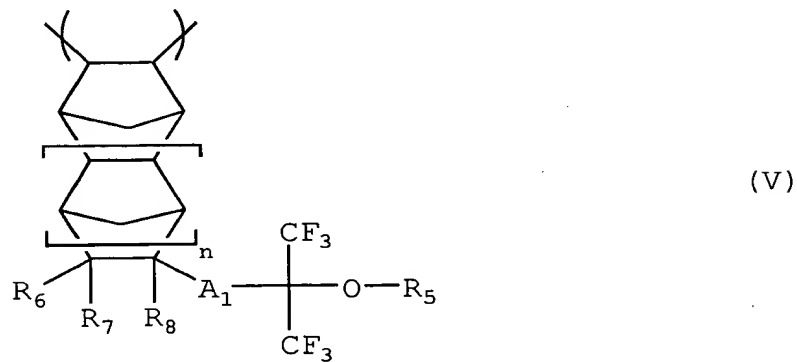
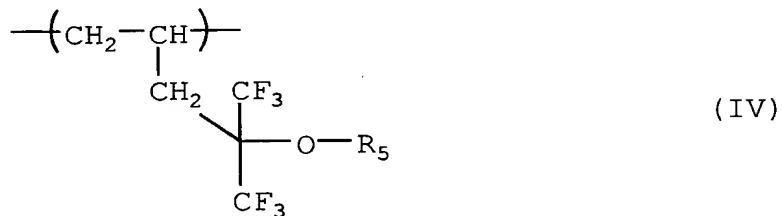
(B) a compound capable of generating an acid upon irradiation with one of an actinic ray and radiation; and

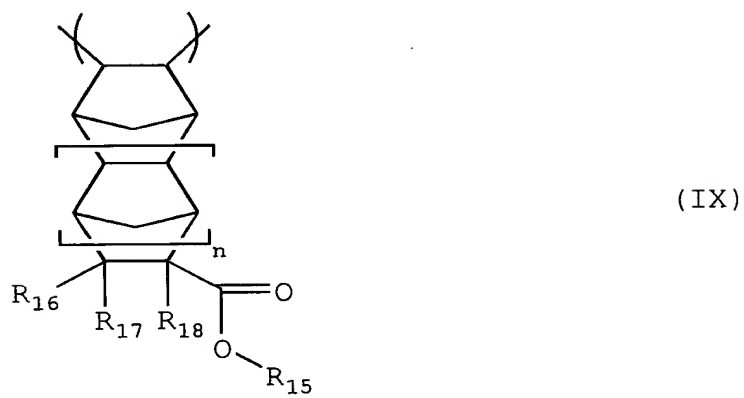
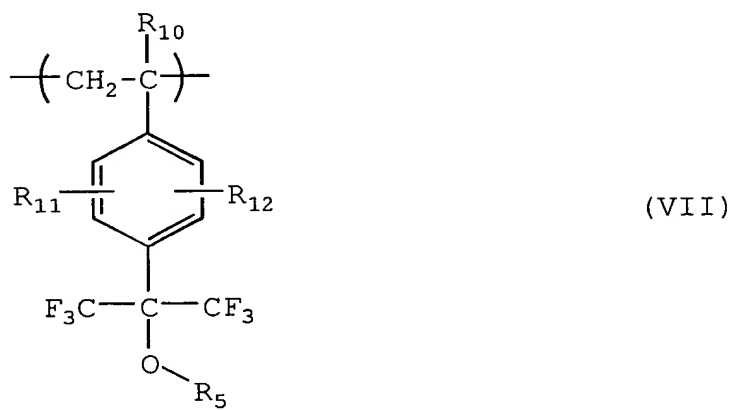
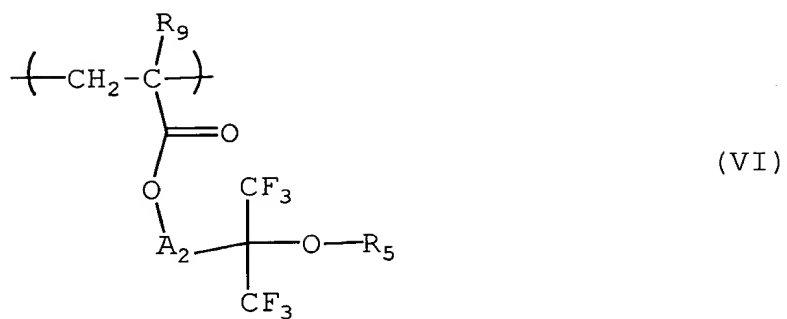
(C) a surfactant containing at least one of a silicon atom and fluorine atom.

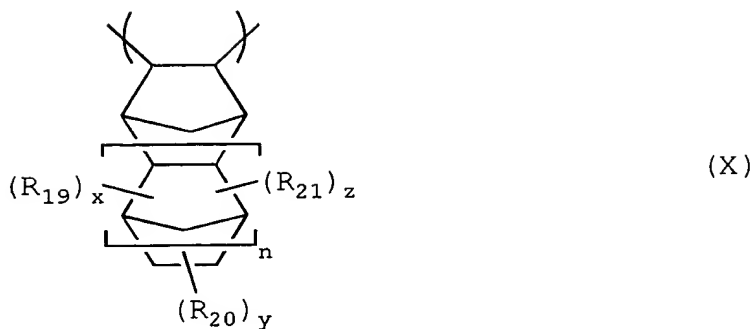
(2) The positive resist composition as described in item (1), wherein the resin (A) comprises one of a fluorine group-containing resin having at least one selected from a perfluoroalkylene group and a perfluoroarylene group, as a part or all of the main chain of the polymer skeleton; and a fluorine group-containing resin having at least one selected from a perfluoroalkyl group, a perfluoroaryl group, a hexafluoro-2-propanol group and a group wherein the OH group in a hexafluoro-2-propanol group is protected, as a part or all of the side chain of the polymer skeleton.

(3) The positive resist composition as described in item (1) or (2) , wherein the resin (A) comprising one of a resin containing at least one of repeating units represented by formulae (I) to (III); a resin containing at

least one of repeating units represented by formulae (IV) to (VII); or a resin containing at least one of repeating units represented by formulae (VIII) to (X):







wherein R_0 and R_1 each represents a hydrogen atom, a fluorine atom, or an alkyl, perfluoroalkyl, cycloalkyl or aryl group, each of which may have a substituent;

R_2 to R_4 each represents an alkyl, perfluoroalkyl, cycloalkyl or aryl group, each of which may have a substituent and R_0 and R_1 may combine to form a ring, R_0 and R_2 may combine to form a ring and R_3 and R_4 may combine to form a ring;

R_5 represents a hydrogen atom, an alkyl, perfluoroalkyl, monocyclic or polycyclic cycloalkyl, acyl or alkoxy carbonyl group, each of which may have a substituent;

R_6 , R_7 and R_8 , which may be the same or different, each represents a hydrogen atom, a halogen atom or an alkyl, perfluoroalkyl or alkoxy group, each of which may have a substituent;

R_9 and R_{10} , which may be the same or different, each represents a hydrogen atom, a halogen atom, a cyano group, or an alkyl or haloalkyl group, each of which may have a substituent;

R_{11} and R_{12} , which may be the same or different, each

represents a hydrogen atom, a hydroxyl group, a halogen atom, a cyano group, an alkoxy group, an acyl group, or an alkyl, cycloalkyl, alkenyl, aralkyl or aryl group, and the alkyl, the cycloalkyl, the alkenyl, the aralkyl or the aryl group each may have a substituent;

R_{13} and R_{14} , which may be the same or different, each represents a hydrogen atom, a halogen atom, a cyano group, or an alkyl or haloalkyl, each of which may have a substituent;

R_{15} represents an alkyl, monocyclic or polycyclic cycloalkyl, alkenyl, aralkyl or aryl group, each of which has a fluorine atom;

R_{16} , R_{17} and R_{18} , which may be the same or different, each represents a hydrogen atom, a halogen atom, a cyano group, or an alkyl, perfluoroalkyl, alkoxy or $-CO-O-R_{15}$ group, each of which may have a substituent;

R_{19} , R_{20} and R_{21} , which may be the same or different, each represents a hydrogen atom, a fluorine atom or an alkyl, monocyclic or polycyclic cycloalkyl, alkenyl, aralkyl, aryl or alkoxy group, each of which has a fluorine atom, provided that at least one of R_{19} , R_{20} and R_{21} is a group other than a hydrogen atom;

A_1 and A_2 each represents a single bond, a divalent alkylene, alkenylene, cycloalkylene, arylene group, $-O-CO-$, $R_{22}-$, $-CO-O-R_{23}-$ or $-CO-N(R_{24})-R_{25}-$, and the divalent alkylene,

alkenylene, cycloalkylene or arylene group each may have a substituent;

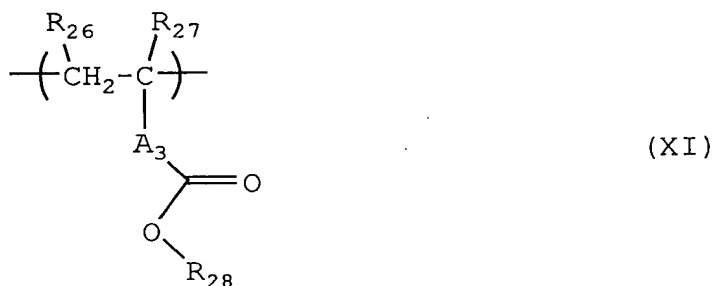
R_{22} , R_{23} and R_{25} , which may be the same or different, each represents a single bond or a divalent alkylene, alkenylene, cycloalkylene or arylene group, each of which may have an ether group, an ester group, an amide group, a urethane group or a ureido group;

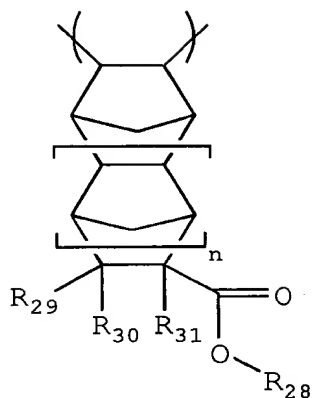
R_{24} represents a hydrogen atom or an alkyl, cycloalkyl, aralkyl or aryl group, each of which may have a substituent;

n represents 0 or 1; and

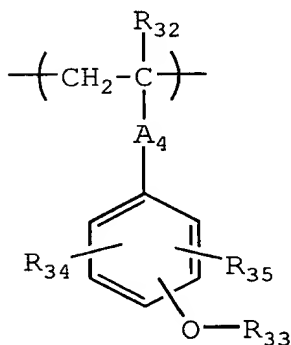
x , y and z each represents an integer of 0 to 4.

(4) The positive resist composition as described in any one of items (1) to (3), wherein the resin (A) contains at least one of repeating units represented by formulae (XI) to (XIII):





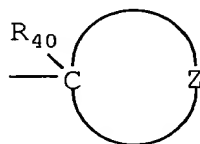
(XII)



(XIII)

wherein R_{26} , R_{27} and R_{32} , which may be the same or different, each represents a hydrogen atom, a halogen atom, a cyano group, or an alkyl or haloalkyl group, each of which may have a substituent;

R_{28} and R_{33} each represents $-C(R_{36})(R_{37})(R_{38})$, $-C(R_{36})(R_{37})(OR_{39})$ or a group represented by formula (XIV):



(XIV)

wherein R_{29} , R_{30} and R_{31} , which may be the same or different, each represents a hydrogen atom, a halogen atom, a cyano group or an alkyl, perfluoroalkyl, alkoxy or $-CO-O-R_{28}$ group,

each of which may have a substituent;

R₃₄ and R₃₅, which may be the same or different, each represents a hydrogen atom, a hydroxyl group, a halogen atom, a cyano group, an alkoxy group, an acyl group, or an alkyl, cycloalkylene, alkenyl, aralkyl or aryl group, and the alkyl, cycloalkylene, alkenyl, aralkyl or aryl group each may have a substituent;

R₃₆, R₃₇, R₃₈ and R₃₉, which may be the same or different, each represents an alkyl, cycloalkyl, alkenyl, aralkyl or aryl group, each of which may have a substituent, and two of R₃₆, R₃₇ and R₃₈, or two of R₃₆, R₃₇ and R₃₉ may combine to form a ring;

R₄₀ represents an alkyl, cycloalkyl, alkenyl, alkynyl, aralkyl or aryl group, each of which may have a substituent;

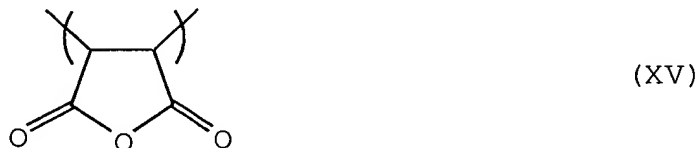
A₃ and A₄ each represents a single bond, a divalent alkylene, alkenylene, cycloalkylene, arylene group, -O-CO-R₂₂-, -CO-O-R₂₃- or -CO-N(R₂₄)-R₂₅-, and the divalent alkylene, alkenylene, cycloalkylene or arylene group each may have a substituent;

R₂₂ to R₂₅ have the same meanings as above;

Z represents an atomic group constituting a monocyclic or polycyclic alicyclic group together with the carbon atom; and

n represents 0 or 1.

(5) The positive composition as described in any one of items (1) to (4), wherein the resin (A) contains at least one of repeating units represented by formulae (XV) and (XVI):



wherein R_{41} represents an alkyl, cycloalkyl, aralkyl or aryl group, each of which may have a substituent.

(6) The positive resist composition as described in any of items (1) to (5), which further comprises a compound (D) containing a basic nitrogen atom as an acid diffusion inhibitor.

(7) The positive resist composition as described in any one of items (1) to (6), wherein the compound (B) comprises at least one compound selected from sulfonium salt compounds and iodonium salt compounds capable of generating, upon irradiation with one of an actinic ray and radiation, at least one of a perfluoroalkylsulfonic acid having 2 or more carbon atoms; a perfluoroarylsulfonic

acid; and an arylsulfonic acid having a perfluoroalkyl group as a substituent.

(8) The positive resist composition as described in any one of items (1) to (7), which is a composition to be irradiated with an ultraviolet ray having a wave length of 160 nm or less.

[Mode for Carrying Out the Invention]

The compounds for use in the present invention are described in detail below.

[1] Fluorine group-containing resin (A) of the present invention

The fluorine group-containing resin (A) for use in the present invention is a resin characterized by having on the main chain and/or the side chain of the polymer a structure such that the fluorine atom is substituted, and having a group capable of decomposing under the action of an acid to increase the solubility in an alkali developer. This is preferably a fluorine group-containing resin having on the main chain of the polymer skeleton at least one site selected from a perfluoroalkylene group and a perfluoroarylene group, or a fluorine group-containing resin having on the side chain of the polymer skeleton at least one site selected from a perfluoroalkyl group, a perfluoroaryl group,

a hexafluoro-2-propanol group and a group resulting from protecting the OH group of a hexafluoro-2-propanol group.

To speak specifically, this is one of a resin having at least one of repeating units represented by formulae (I) to (III), a resin having at least one of repeating units represented by formulae (IV) to (VII), or a resin having at least one of repeating units represented by formulae (VIII) to (X); more preferably a fluorine group-containing resin containing an acid-decomposable group having at least one of repeating units represented by formulae (XI) to (XIII).

Also, for controlling the physical properties of the fluorine group-containing resin, such as hydrophilicity/hydrophobicity, glass transition point and transmittance to exposure light or for controlling the polymerizability on the synthesis of polymer, the resin may have at least one repeating unit derived from a maleic anhydride, or a vinyl ether, each of which is represented by formula (XV) or (XVI).

In formulae, R_0 and R_1 each represents a hydrogen atom, a fluorine atom or an alkyl, perfluoroalkyl, cycloalkyl or aryl group, each of which may have a substituent.

R_2 to R_4 each represents an alkyl, perfluoroalkyl, cycloalkyl or aryl group, each of which may have a substituent. Also, each of the pairs R_0 and R_1 , R_0 and R_2 , and R_3 and R_4 may combine to form a ring.

R₅ represents a hydrogen atom or an alkyl, perfluoroalkyl, a monocyclic or polycyclic cycloalkyl, acyl or alkoxycarbonyl group, each of which may have a substituent.

R₆, R₇ and R₈, which may be the same or different, each represents a hydrogen atom, a halogen atom or an alkyl, perfluoroalkyl or alkoxy group, each of which may have a substituent.

R₉ and R₁₀, which may be the same or different, each represents a hydrogen atom, a halogen atom, a cyano group or an alkyl or haloalkyl group, each of which may have a substituent.

R₁₁ and R₁₂, which may be the same or different, each represents a hydrogen atom, a hydroxyl group, a halogen atom, a cyano group, an alkoxy group, an acyl group or an alkyl, cycloalkyl, alkenyl, aralkyl or aryl group, and the alkyl, the cycloalkyl, the alkenyl, the aralkyl, or the aryl group each may have a substituent.

R₁₃ and R₁₄, which may be the same or different, each represents a hydrogen atom, a halogen atom, a cyano group or an alkyl or haloalkyl group, each of which may have a substituent.

R₁₅ represents an alkyl, monocyclic or polycyclic cycloalkyl, alkenyl, aralkyl or aryl group, each of which has a fluorine atom.

R₁₆, R₁₇ and R₁₈, which may be the same or different, each represents a hydrogen atom, a halogen atom, a cyano group, a cyano group or an alkyl, perfluoroalkyl, alkoxy or -CO-O-R₁₅ group, each of which may have a substituent.

R₁₉, R₂₀ and R₂₁, which may be the same or different, each represents a hydrogen atom, a fluorine atom or an alkyl, monocyclic or polycyclic cycloalkyl, alkenyl, aralkyl, aryl or alkoxy group, each of which has a fluorine atom. However, at least one of R₁₉, R₂₀ and R₂₁ is a group other than a hydrogen atom.

A₁ and A₂ each represents a single bond, a divalent alkylene, alkenylene, cycloalkylene or arylene group, -O-CO-R₂₂-, -CO-O-R₂₃- or -CO-N(R₂₄)-R₂₅-, and the divalent alkylene, alkenylene, cycloalkylene or arylene group each may have a substituent.

R₂₂, R₂₃ and R₂₅, which may be the same or different, each represents a single bond or a divalent alkylene, alkenylene, cycloalkylene or arylene group, each of which may have an ether group, an ester group, an amide group, a urethane group or a ureido group. R₂₄ represents a hydrogen atom or an alkyl, cycloalkyl, aralkyl or aryl group, each of which may have a substituent.

R₂₆, R₂₇ and R₃₂, which may be the same or different, each represents a hydrogen atom, a halogen atom, a cyano group or an alkyl or haloalkyl group, each of which may

have a substituent.

R_{28} and R_{33} each represents $-C(R_{36})(R_{37})(R_{38})$, $-C(R_{36})(R_{37})(OR_{39})$ or a group represented by the above-described formula (XIV).

R_{29} , R_{30} and R_{31} , which may be the same or different, each represents a hydrogen atom, a halogen atom, a cyano group or an alkyl, perfluoroalkyl, alkoxy or $-CO-O-R_{28}$ group, each of which may have a substituent.

R_{34} and R_{35} , which may be the same or different, each represents a hydrogen atom, a hydroxyl group, a halogen atom, a cyano group, an alkoxy group, an acyl group or an alkyl, cycloalkyl, alkenyl, aralkyl or aryl group, and the alkyl, cycloalkyl, alkenyl, aralkyl or aryl group each may have a substituent.

R_{36} , R_{37} , R_{38} and R_{39} , which may be the same or different, each represents an alkyl, cycloalkyl, alkenyl, alkynyl, aralkyl or aryl group, each of which may have a substituent. Two of R_{36} , R_{37} and R_{38} or two of R_{36} , R_{37} and R_{39} may combine to form a ring. The formed ring may contain an oxo group.

R_{40} represents an alkyl, cycloalkyl, alkenyl, aralkyl or aryl group, each of which may have a substituent.

A_3 and A_4 each represents a single bond, a divalent alkylene, alkenylene, cycloalkylene or arylene group, $-O-CO-R_{22}-$, $-CO-O-R_{23}-$ or $-CO-N(R_{24})-R_{25}-$, and the divalent alkylene, alkenylene, cycloalkylene or arylene group each

may have a substituent, .

Z represents an atomic group constituting a monocyclic or polycyclic alicyclic group together with the carbon atom.

R₄₁ represents an alkyl, cycloalkyl, aralkyl or aryl group, each of which may have a substituent.

n represents 0 or 1, and x, y and z represents an integer of 0 to 4.

The alkyl group is, for example, an alkyl group having from 1 to 8 carbon atoms and specific preferred examples thereof include a methyl group, an ethyl group, a propyl group, an n-butyl group, a sec-butyl group, a hexyl group, a 2-ethylhexyl group and an octyl group.

The cycloalkyl group may be monocyclic or polycyclic. The monocyclic cycloalkyl group is a cycloalkyl group having from 3 to 8 carbon atoms and preferred examples thereof include a cyclopropyl group, a cyclopentyl group, a cyclohexyl group, a cycloheptyl group and a cyclooctyl group. The polycyclic cycloalkyl group is a cycloalkyl group having from 6 to 20 carbon atoms and preferred examples thereof include an adamantyl group, a norbornyl group, an isoboronyl group, a camphanyl group, a dicyclopentyl group, an a-pinel group, a tricyclodecanyl group, a tetracyclododecyl group and an androstanyl group. However, in the monocyclic or polycyclic alkyl group, the carbon atom may be substituted by a hetero atom such as

oxygen atom.

The perfluoroalkyl group is, for example, a perfluoroalkyl group having from 4 to 12 carbon atoms and specific preferred examples thereof include a perfluorobutyl group, a perfluorohexyl group, a perfluorooctyl group, a perfluorooctylethyl group and a perfluorododecyl group.

The haloalkyl group is, for example, a haloalkyl group having from 1 to 4 carbon atoms and specific preferred examples thereof include a chloromethyl group, a chloroethyl group, a chloropropyl group, a chlorobutyl group, a bromomethyl group and a bromoethyl group.

The aryl group is, for example, an aryl group having from 6 to 15 carbon atoms and specific preferred examples thereof include a phenyl group, a tolyl group, a dimethylphenyl group, a 2,4,6-trimethylphenyl group, a naphthyl group, an anthryl group and a 9,10-dimethoxyanthryl group.

The aralkyl group is, for example, an aralkyl group having from 7 to 12 carbon atoms and specific preferred examples thereof include a benzyl group, a phenethyl group and a naphthylmethyl group.

The alkenyl group is, for example, an alkenyl group having from 2 to 8 carbon atoms and specific preferred examples thereof include a vinyl group, an allyl group, a

butenyl group and a cyclohexenyl group.

The alkoxy group is, for example, an alkoxy group having from 1 to 8 carbon atoms and specific preferred examples thereof include a methoxy group, an ethoxy group, an n-propoxy group, an iso-propoxy group, a butoxy group, a pentoxy group, an allyloxy group and an octoxy group.

The acyl group is, for example, an acyl group having from 1 to 10 carbon atoms and specific preferred examples thereof include a formyl group, an acetyl group, a propanoyl group, a butanoyl group, a pivaloyl group, an octanoyl group and a benzoyl group.

Examples of the alkoxycarbonyl group include an i-propoxycarbonyl group, a tert-butoxycarbonyl group, a tert-amylloxycarbonyl group and a 1-methyl-1-cyclohexyloxy-carbonyl group. The alkoxycarbonyl group is preferably a secondary alkoxycarbonyl group, more preferably a tertiary alkoxycarbonyl group.

The alkylene group is preferably an alkylene group having from 1 to 8 carbon atoms, such as methylene group, ethylene group, propylene group, butylene group, hexylene group and octylene group, each of which may have a substituent.

The alkenylene group is preferably an alkenylene group having from 2 to 6 carbon atoms, such as ethenylene group, propenylene group and butenylene group, each of which may

have a substituent.

The cycloalkylene group is preferably a cycloalkylene group having from 5 to 8 carbon atoms, such as cyclopentylene group and cyclohexylene group, each of which may have a substituent.

The arylene group is preferably an arylene group having from 6 to 15 carbon atoms, such as phenylene group, tolylene group and naphthylene group, each of which may have a substituent.

The ring formed resulting from R_0 and R_1 , R_0 and R_2 , or R_3 and R_4 combining with each other is, for example, a 5-, 6- or 7-membered ring and specific examples thereof include a pentane ring, a hexane ring, a furan ring, a dioxanol ring and a 1,3-dioxolan ring, which are each substituted by fluorine.

The ring formed resulting from two of R_{36} to R_{38} or two of R_{36} to R_{37} and R_{39} combining with each other is, for example, a 3-, 4-, 5-, 6-, 7- or 8-membered ring and specific preferred examples thereof include a cyclopropane ring, a cyclopentane ring, a cyclohexane ring, a furan ring and a pyran ring.

Z represents an atomic group constituting a monocyclic or polycyclic alicyclic group. In the case of a monocyclic group, the formed alicyclic group is an alicyclic group having from 3 to 8 carbon atoms and preferred examples

thereof include a cyclopropyl group, a cyclopentyl group, a cyclohexyl group, a cycloheptyl group and a cyclooctyl group. In the case of a polycyclic group, the formed alicyclic group is an alicyclic group having from 6 to 20 carbon atoms and preferred examples thereof include an adamantyl group, a norbornyl group, an isoboronyl group, a camphanyl group, a dicyclopentyl group, an a-pinyl group, a tricyclodecanyl group, a tetracyclododecyl group and an androstanyl group.

Examples of the substituent substituted to these groups include substituents having active hydrogen, such as alkyl group, cycloalkyl group, aryl group, amino group, amido group, ureido group, urethane group, hydroxyl group and carboxyl group, a halogen atom (e.g., fluorine, chlorine, bromine, iodine), an alkoxy group (e.g., methoxy, ethoxy, propoxy, butoxy), a thioether group, an acyl group (e.g., acetyl, propanoyl, benzoyl), an acyloxy group (e.g., acetoxyl, propanoyloxy, benzoyloxy), an alkoxycarbonyl group (e.g., methoxycarbonyl, ethoxycarbonyl, propoxycarbonyl), a cyano group and a nitro group.

Examples of the alkyl group, the cycloalkyl group and the aryl group include those described above, but the alkyl group may further be substituted by a fluorine atom or a cycloalkyl group.

Examples of the group capable of decomposing under the

action of an acid to show alkali solubility, contained in the fluorine group-containing resin for use in the present invention, include $-O-C(R_{36})(R_{37})(R_{38})$, $-O-C(R_{36})(R_{37})(OR_{39})$, $-O-COO-C(R_{36})(R_{37})(R_{38})$, $-O-C(R_{01})(R_{02})COO-C(R_{36})(R_{37})(R_{38})$, $-COO-C(R_{36})(R_{37})(R_{38})$ and $-COO-C(R_{36})(R_{37})(OR_{39})$ (wherein R_{36} to R_{39} have the same meanings as above, and R_{01} and R_{02} each represents a hydrogen atom or the above-described alkyl, cycloalkyl, alkenyl, aralkyl or aryl group, each of which may have a substituent).

Specific preferred examples thereof include an ether or ester group of a tertiary alkyl group such as tert-butyl group, tert-amyl group, 1-alkyl-1-cyclohexyl group, 2-alkyl-2-adamantyl group, 2-adamantyl-2-propyl group and 2-(4-methylcyclohexyl)-2-propyl group, an acetal or acetal ester group such as 1-alkoxy-1-ethoxy group and tetrahydropyranyl group, a tert-alkylcarbonate group and a tert-alkylcarbonylmethoxy group.

The total content of the repeating units represented by formulae (I) to (X) is generally from 10 to 80 mol%, preferably from 30 to 70 mol%, more preferably from 35 to 65 mol%, in the entire polymer composition.

The content of the repeating unit represented by formulae (XI) to (XIII) is generally from 0 to 70 mol%, preferably from 10 to 60 mol%, more preferably from 20 to 50 mol%, in the entire polymer composition.

In the resin (A) for use in the present invention, in addition to the above-described repeating structural units, another polymerizable monomer may also be copolymerized so as to improve the performance of the positive resist of the present invention.

Examples of the copolymerizable monomer which can be used include compounds having one addition-polymerizable unsaturated bond, selected from acrylic acid esters other than those described above, acrylamides, methacrylic acid esters, methacrylamides, allyl compounds, vinyl ethers, vinyl esters, styrenes and crotonic acid esters.

Specific examples thereof include acrylic acid esters such as alkyl (the alkyl group is preferably an alkyl group having from 1 to 10 carbon atoms) acrylate (e.g., methyl acrylate, ethyl acrylate, propyl acrylate, tert-butyl acrylate, amyl acrylate, cyclohexyl acrylate, ethylhexyl acrylate, octyl acrylate, tert-octyl acrylate, chloroethyl acrylate, 2-hydroxyethyl acrylate, 2,2-dimethylhydroxypropyl acrylate, 5-hydroxypentyl acrylate, trimethylolpropane monoacrylate, pentaerythritol monoacrylate, glycidyl acrylate, benzyl acrylate, furfuryl acrylate, tetrahydrofurfuryl acrylate) and aryl acrylate (e.g., phenyl acrylate);

methacrylic acid esters such as alkyl (the alkyl group is preferably an alkyl group having from 1 to 10 carbon

atoms) methacrylate (e.g., methyl methacrylate, ethyl methacrylate, propyl methacrylate, isopropyl methacrylate, tert-butyl methacrylate, amyl methacrylate, hexyl methacrylate, cyclohexyl methacrylate, benzyl methacrylate, chlorobenzyl methacrylate, octyl methacrylate, 2-hydroxyethyl methacrylate, 4-hydroxybutyl methacrylate, 5-hydroxypentyl methacrylate, 2,2-dimethyl-3-hydroxypropyl methacrylate, trimethylolpropane monomethacrylate, pentaerythritol monomethacrylate, glycidyl methacrylate, furfuryl methacrylate, tetrahydrofurfuryl methacrylate) and aryl methacrylate (e.g., phenyl methacrylate, cresyl methacrylate, naphthyl methacrylate);

acrylamides such as acrylamide, N-alkylacrylamide (the alkyl group is an alkyl group having from 1 to 10 carbon atoms, such as methyl group, ethyl group, propyl group, butyl group, tert-butyl group, heptyl group, octyl group, cyclohexyl group, benzyl group, hydroxyethyl group and benzyl group), N-arylacrylamide (the aryl group is, for example, a phenyl group, a tolyl group, a nitrophenyl group, a naphthyl group, a cyanophenyl group, a hydroxyphenyl group or a carboxyphenyl group), N,N-dialkylacrylamide (the alkyl group is an alkyl group having from 1 to 10 carbon atoms, such as methyl group, ethyl group, butyl group, isobutyl group, ethylhexyl group and cyclohexyl group), N,N-diarylacrylamide (the aryl group is, for example, a

phenyl group), N-methyl-N-phenylacrylamide, N-hydroxyethyl-N-methylacrylamide and N-2-acetamidoethyl-N-acetylacrylamide;

methacrylamides such as methacrylamide, N-alkylmethacrylamide (the alkyl group is an alkyl group having from 1 to 10 carbon atoms, such as methyl group, ethyl group, tert-butyl group, ethylhexyl group, hydroxyethyl group and cyclohexyl group), N-arylmethacrylamide (the aryl group is, for example, a phenyl group), N,N-dialkylmethacrylamide (the alkyl group is, for example, an ethyl group, a propyl group or a butyl group), N,N-diarylmethacrylamide (the aryl group is, for example, a phenyl group), N-hydroxyethyl-N-methylmethacrylamide, N-methyl-N-phenylmethacrylamide and N-ethyl-N-phenylmethacrylamide; allyl compounds such as allyl ester (e.g., allyl acetate, allyl caproate, allyl caprate, allyl laurate, allyl palmitate, allyl stearate, allyl benzoate, allyl acetoacetate, allyl lactate) and allyloxy ethanol;

vinyl ethers such as alkyl vinyl ether (e.g., hexyl vinyl ether, octyl vinyl ether, decyl vinyl ether, ethylhexyl vinyl ether, methoxyethyl vinyl ether, ethoxyethyl vinyl ether, chloroethyl vinyl ether, 1-methyl-2,2-dimethylpropyl vinyl ether, 2-ethylbutyl vinyl ether, hydroxyethyl vinyl ether, diethylene glycol vinyl ether,

dimethylaminoethyl vinyl ether, diethylaminoethyl vinyl ether, butylaminoethyl vinyl ether, benzyl vinyl ether, tetrahydrofurfuryl vinyl ether) and vinyl aryl ether (e.g., vinyl phenyl ether, vinyl tolyl ether, vinyl chlorophenyl ether, vinyl-2,4-dichlorophenyl ether, vinyl naphthyl ether, vinyl anthranyl ether);

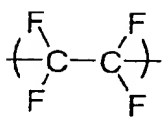
vinyl esters such as vinyl butyrate, vinyl isobutyrate, vinyl trimethyl acetate, vinyl diethyl acetate, vinyl valerate, vinyl caproate, vinyl chloroacetate, vinyl dichloroacetate, vinyl methoxyacetate, vinyl butoxyacetate, vinyl phenylacetate, vinyl acetoacetate, vinyl lactate; vinyl- β -phenylbutyrate, vinylchlorohexyl carboxylate, vinyl benzoate, vinyl salicylate, vinyl chlorobenzoate, vinyl tetrachlorobenzoate and vinyl naphthoate;

styrenes such as styrene, alkylstyrene (e.g., methylstyrene, dimethylstyrene, trimethylstyrene, ethylstyrene, diethylstyrene, isopropylstyrene, butylstyrene, hexylstyrene, cyclohexylstyrene, decylstyrene, benzylstyrene, chloromethylstyrene, trifluoromethylstyrene, ethoxymethylstyrene, acetoxymethylstyrene), alkoxystyrene (e.g., methoxystyrene, 4-methoxy-3-methylstyrene, dimethoxystyrene), halogen styrene (e.g., chlorostyrene, dichlorostyrene, trichlorostyrene, tetrachlorostyrene, pentachlorostyrene, bromostyrene, dibromostyrene, iodostyrene, fluorostyrene, trifluorostyrene, 2-bromo-4-

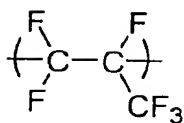
trifluoromethylstyrene, 4-fluoro-3-trifluoromethylstyrene), carboxystyrene and vinyl naphthalene; and

crotonic acid esters such as alkyl crotonate (e.g., butyl crotonate, hexyl crotonate, glycerin monocrotonate); dialkyl itaconates (e.g., dimethyl itaconate, diethyl itaconate, dibutyl itaconate); dialkyl esters of maleic acid or fumaric acid (e.g., dimethyl maleate, dibutyl fumarate), maleic anhydride, maleimide, acrylonitrile, methacrylonitrile and maleylonitrile. In addition, addition-polymerizable unsaturated compounds which can be copolymerized in general may be used.

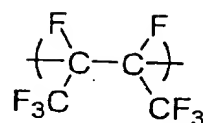
Specific examples of the repeating structural units represented by formulae (I) to (X) are set forth below, however, the present invention is not limited thereto.



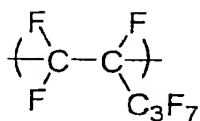
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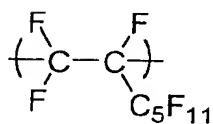
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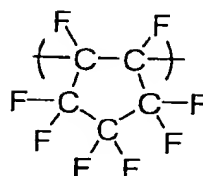
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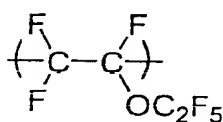
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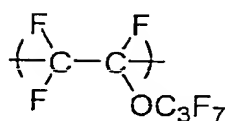
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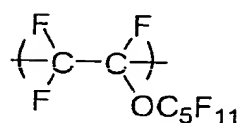
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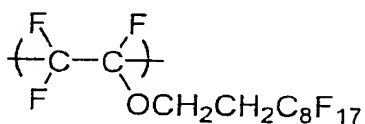
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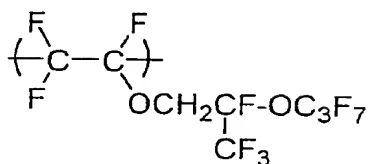
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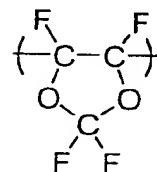
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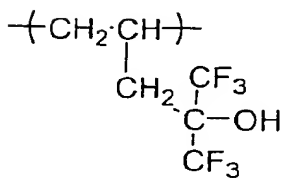
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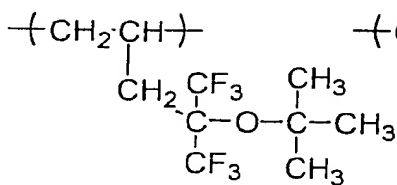
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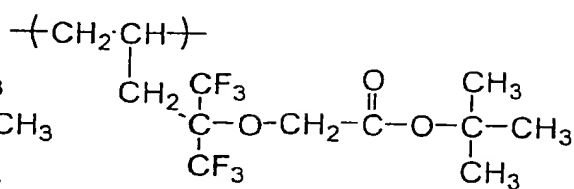
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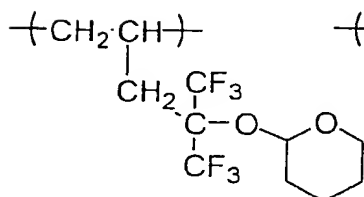
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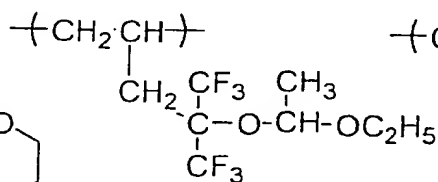
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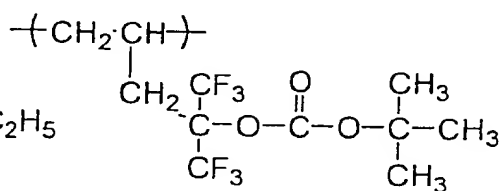
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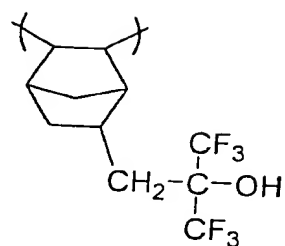
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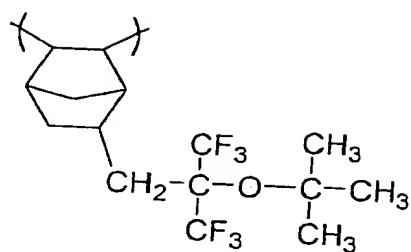
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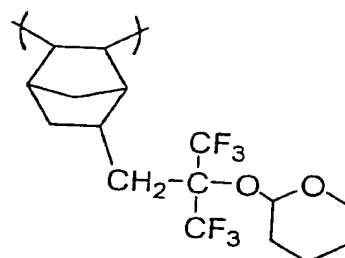
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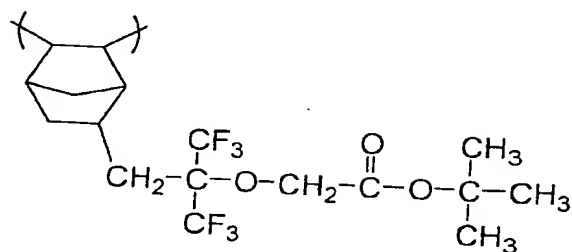
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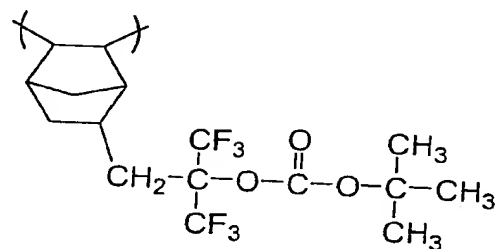
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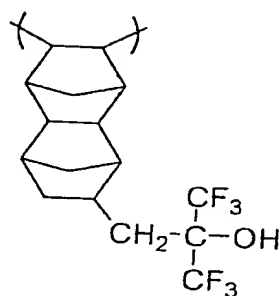
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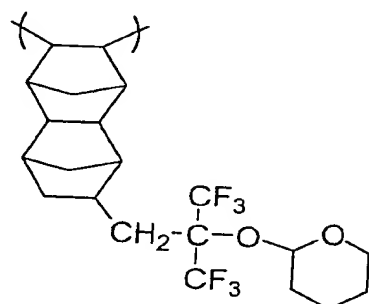
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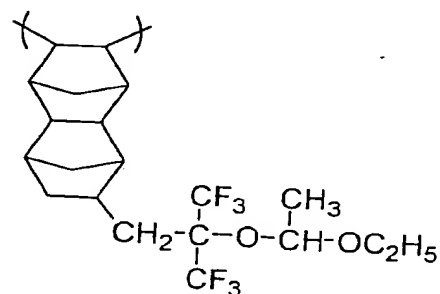
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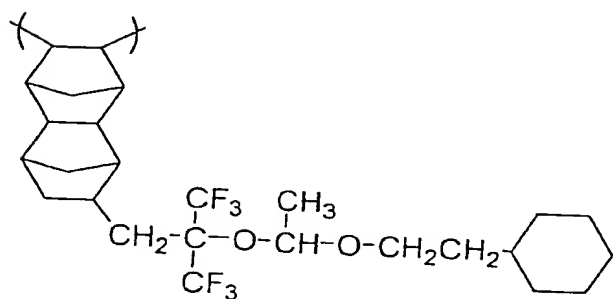
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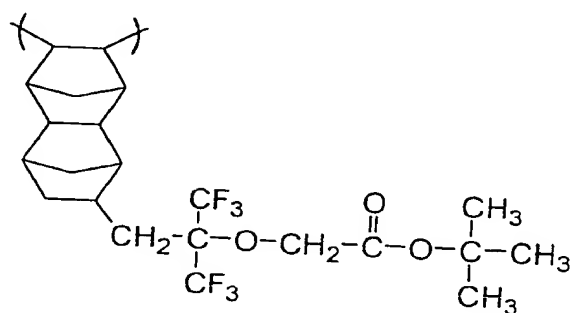
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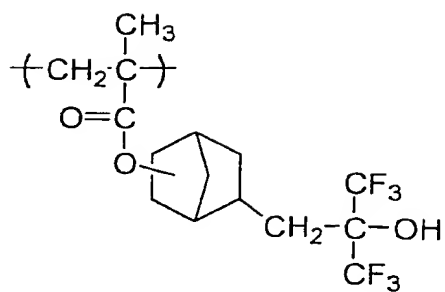
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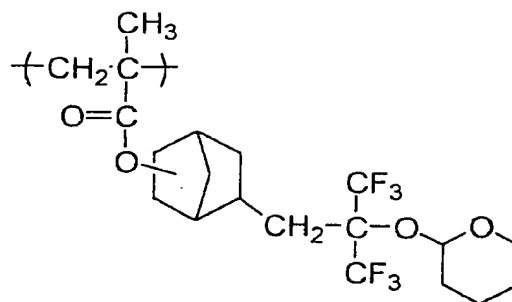
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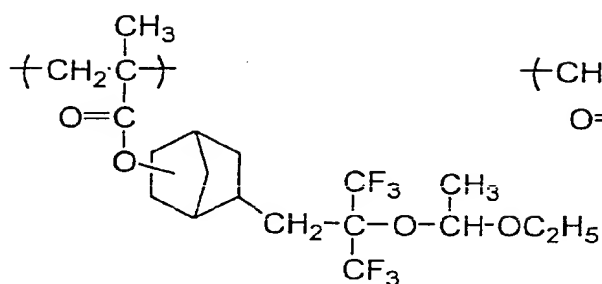
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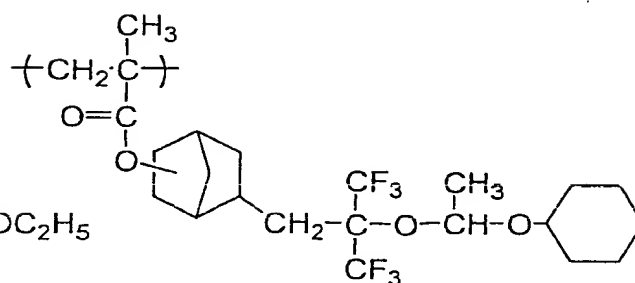
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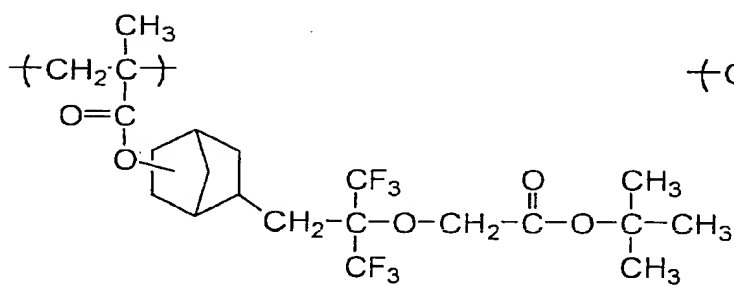
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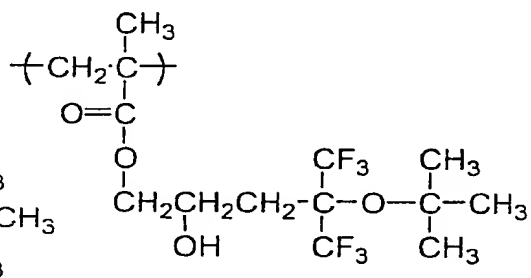
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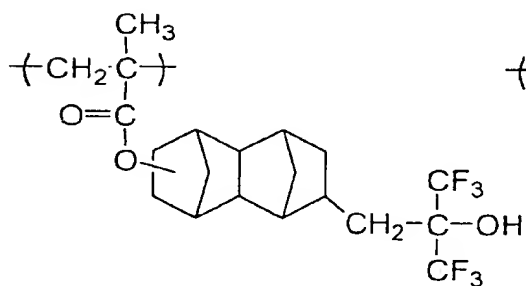
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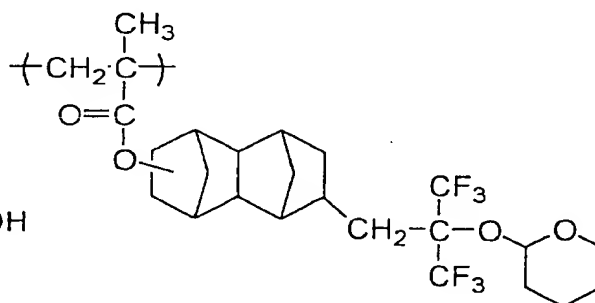
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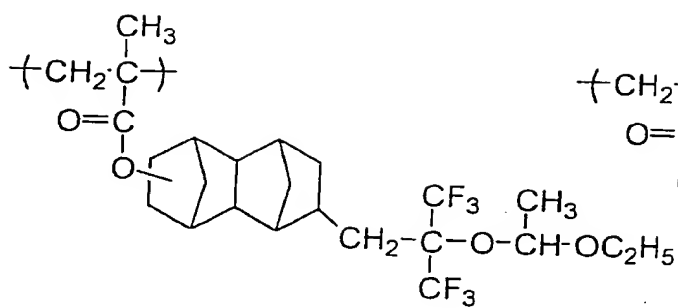
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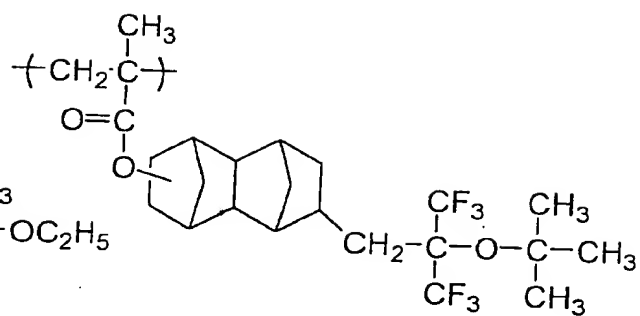
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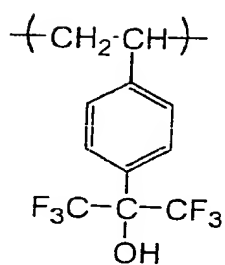
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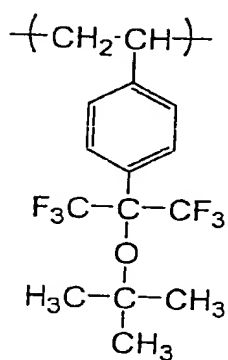
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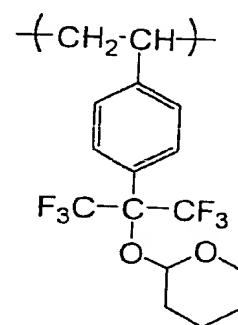
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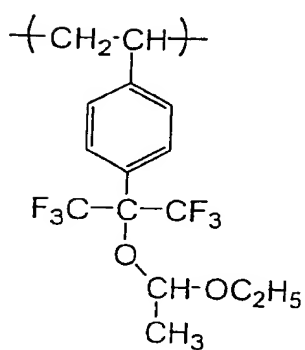
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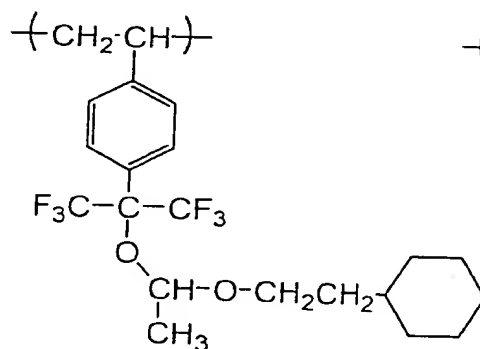
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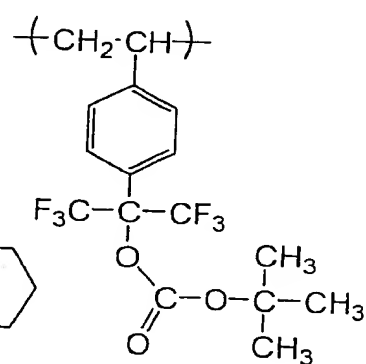
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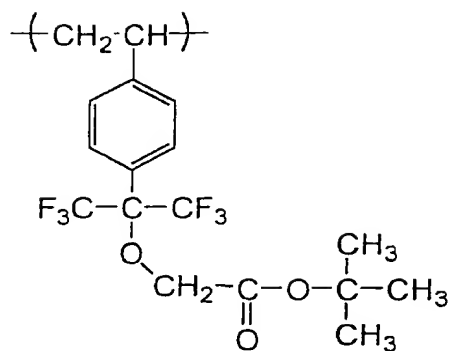
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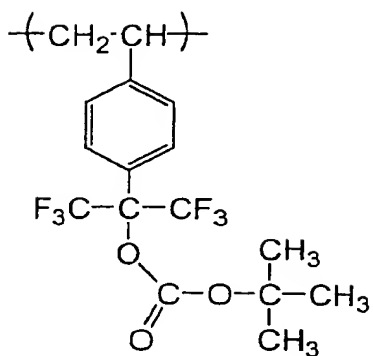
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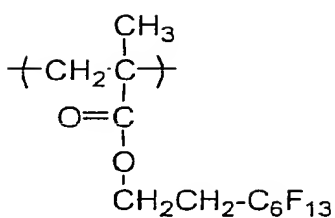
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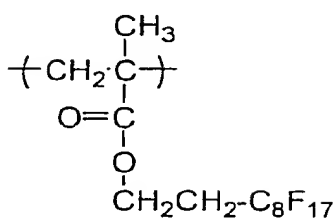
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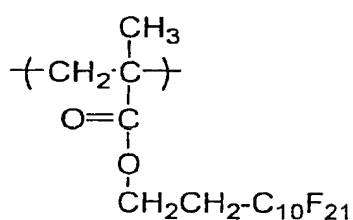
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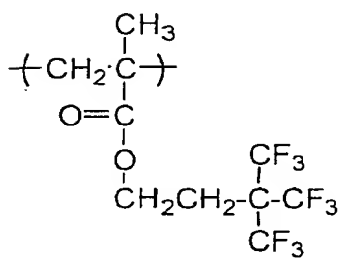
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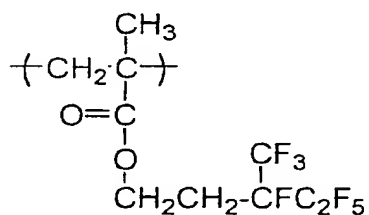
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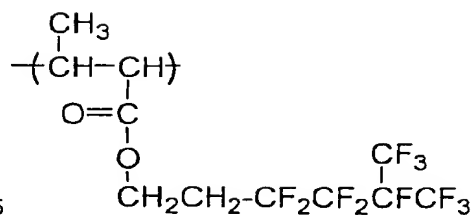
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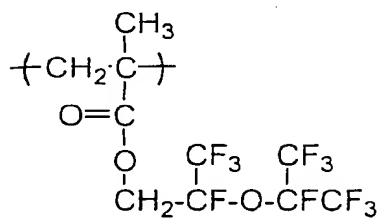
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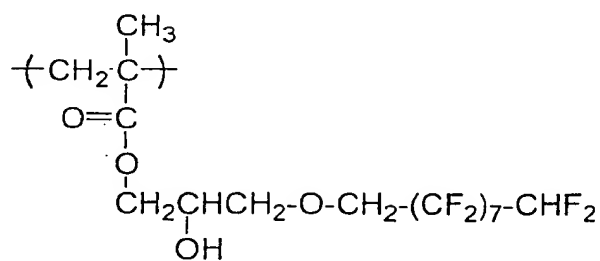
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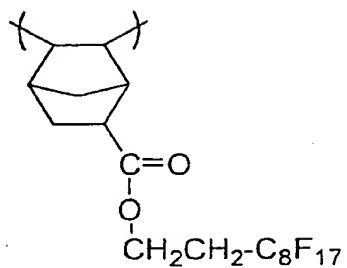
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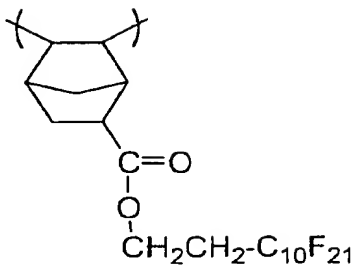
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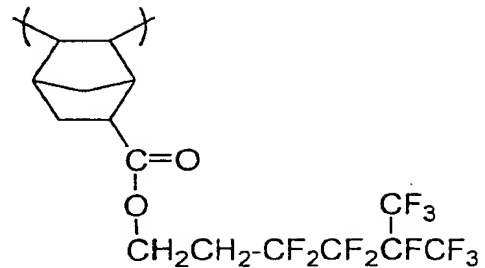
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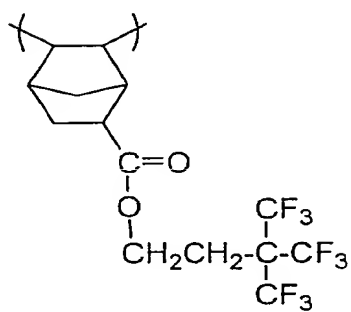
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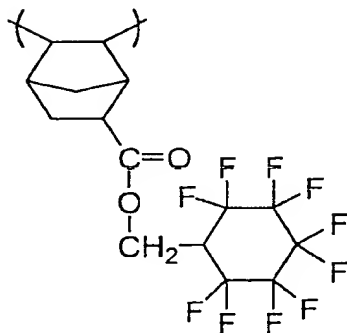
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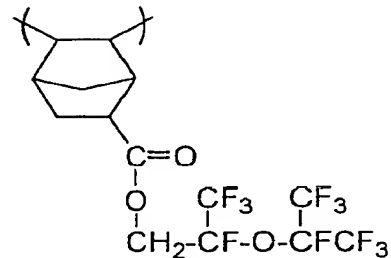
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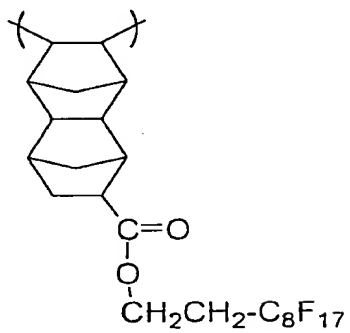
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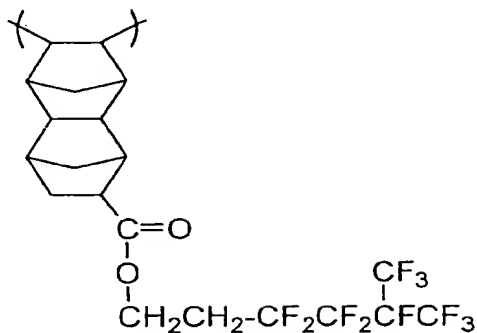
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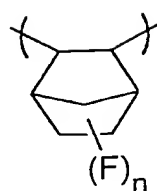
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(F-61)

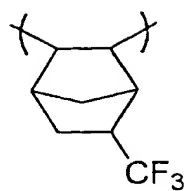


(F-62)

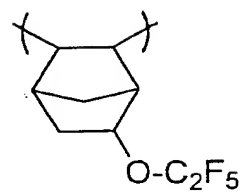


$n=8$

(F-63)

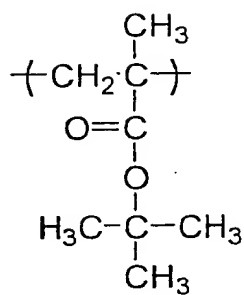


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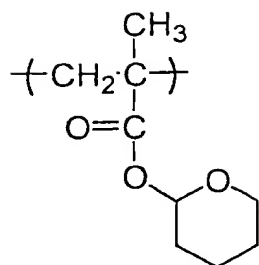


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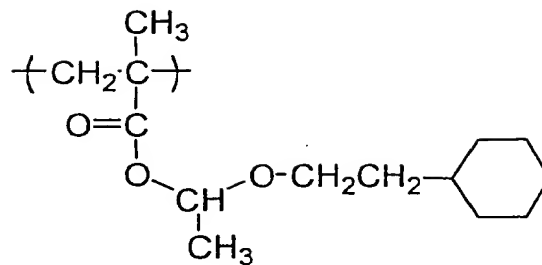
Specific examples of the repeating structural units represented by formulae (XI) to (XIII) are set forth below, however, the present invention is not limited thereto.



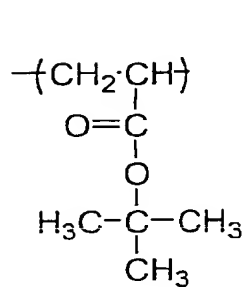
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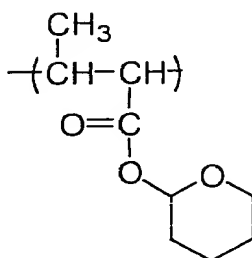
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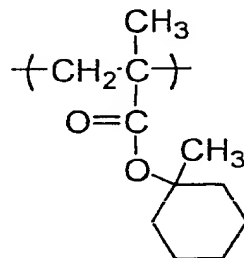
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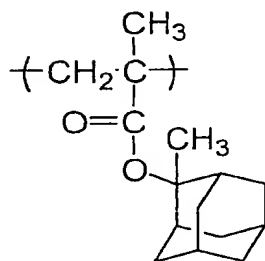
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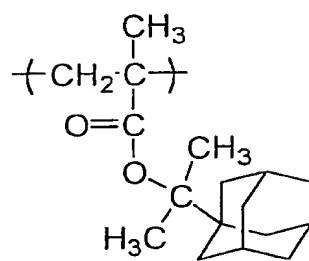
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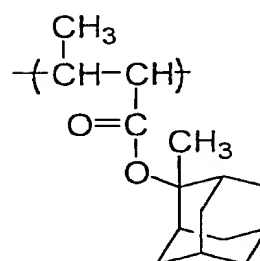
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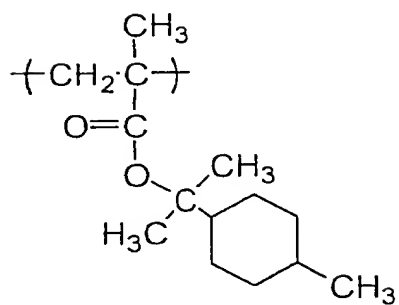
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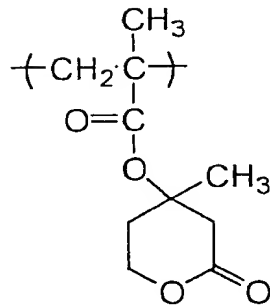
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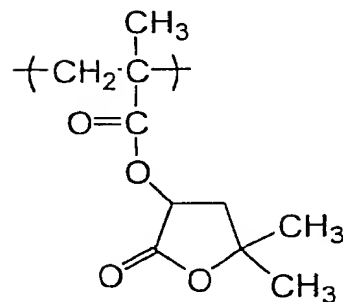
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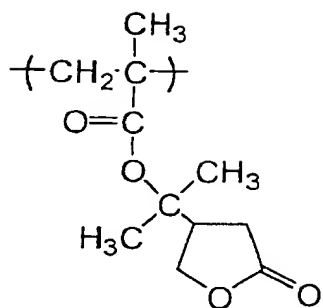
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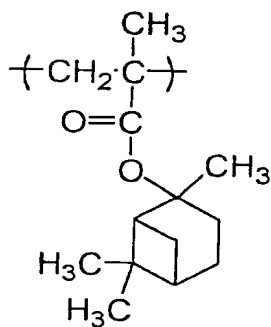
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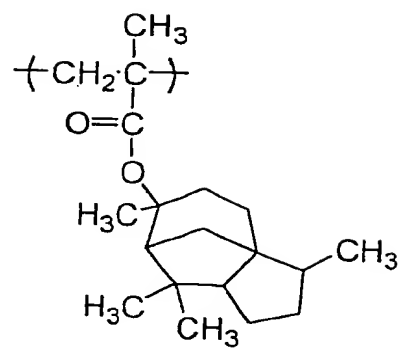
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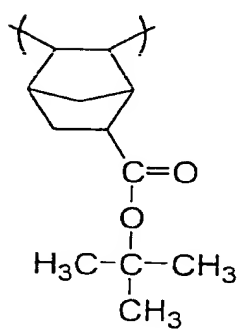
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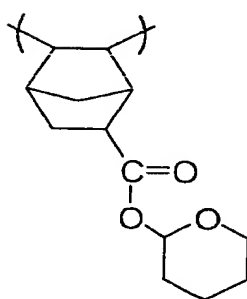
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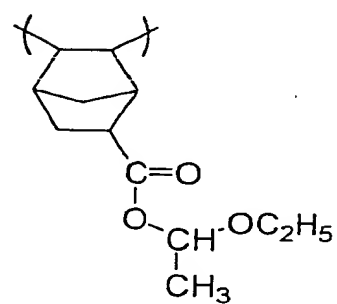
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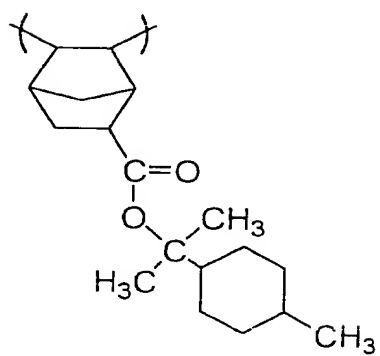
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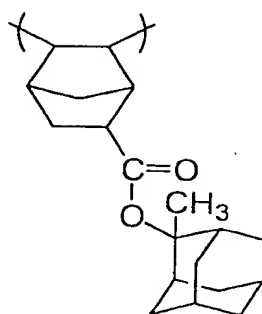
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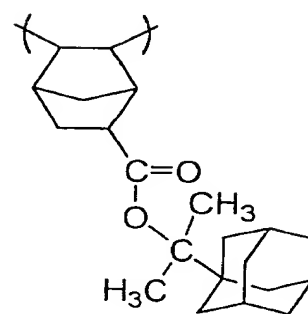
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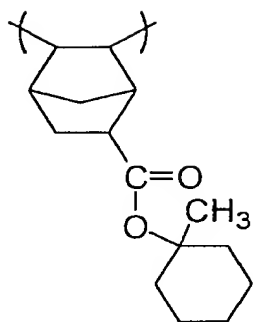
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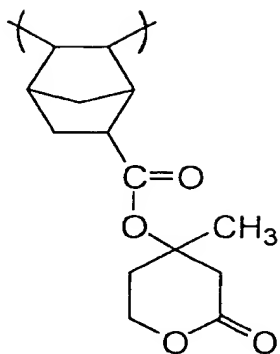
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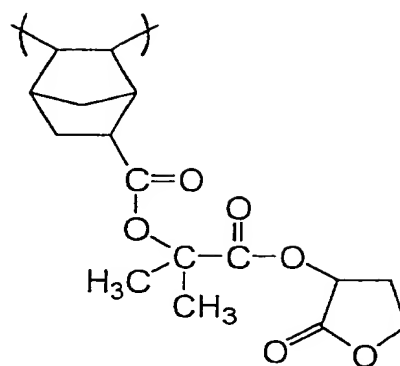
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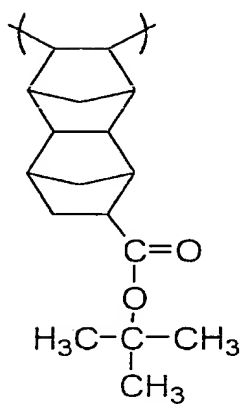
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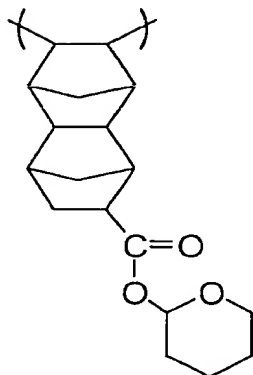
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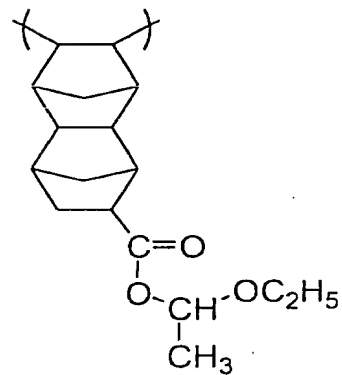
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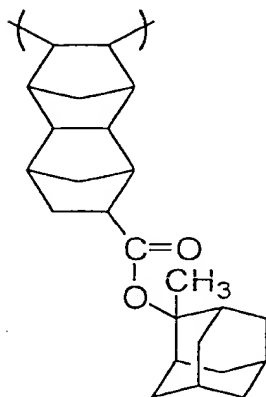
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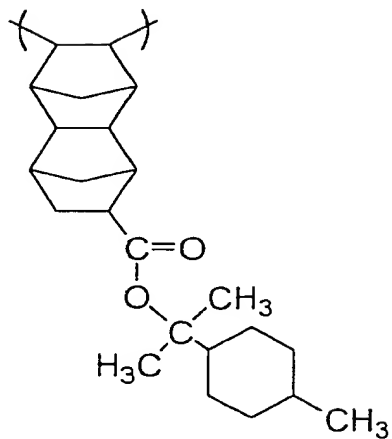
(B-26)



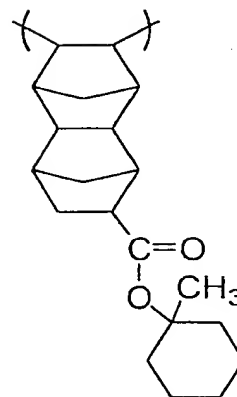
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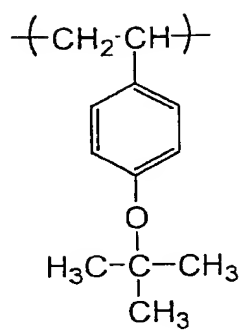
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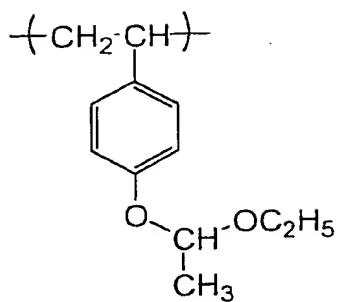
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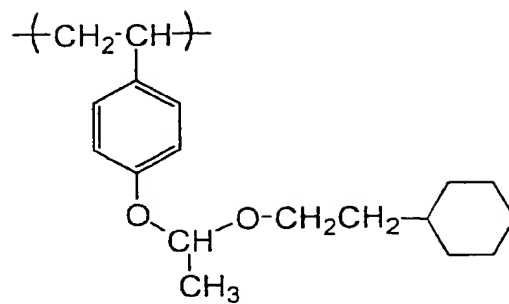
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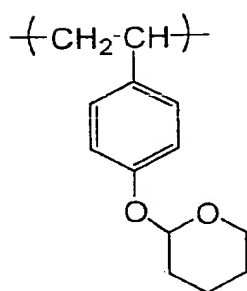
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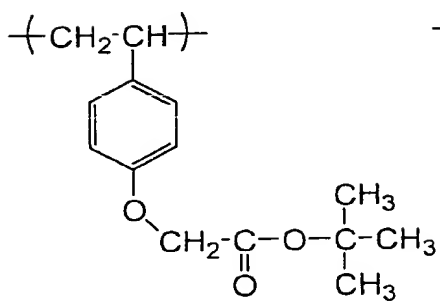
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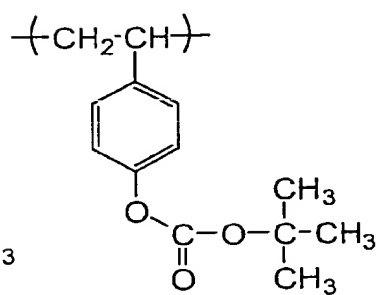
(B-33)



(B-34)



(B-35)



(B-36)

These specific examples of the repeating structural units may be used individually or as a mixture of a plurality of those units.

The resin (A) having the above-described repeating structural units preferably has a weight average molecular weight of 1,000 to 200,000, more preferably from 3,000 to 20,000. The molecular weight distribution is from 1 to 10, preferably from 1 to 3, more preferably from 1 to 2. As the molecular weight distribution is narrower, the resolution is higher, the resist shape is excellent, the side wall of the resist pattern is smoother and the roughness property is superior.

The amount added of the resin (A) for use in the present invention is, based on the solid content of the composition, generally from 50 to 99.5% by weight, preferably from 60 to 98% by weight, more preferably from 65 to 95% by weight.

[2] Compound (B) capable of generating acid upon irradiation with actinic rays or radiation of the present invention

Examples of the compound capable of decomposing upon irradiation with actinic rays or radiation to generate an acid, which is used in the present invention, include a photoinitiator for photocationic polymerization, a

photoinitiator for photoradical polymerization, a photo-decoloring agent for dyes, a photo-discoloring agent and a compound capable of generating an acid upon irradiation with known light used for microresist and the like (for example, ultraviolet or far ultraviolet ray of 200 to 400 nm, preferably g line, h line, i line and a KrF excimer laser ray) or with an ArF excimer laser ray, an electron beam, an X ray, a molecular beam or an ion beam. The compound may be appropriately selected from these and a combination thereof.

Other examples of the compound capable of generating an acid upon irradiation with actinic rays or radiation for use in the present invention include onium salts such as diazonium salts described in S.I. Schlesinger, Photoqr. Sci. Eng., 18, 387 (1974), T.S. Bal et al., Polymer, 21, 423 (1980), etc., ammonium salts described in U.S. Patents 4,069,055, 4,069,056 and Re27,992, JP-A-3-140140, etc., phosphonium salts described in D.C. Necker et al., Macromolecules, 17, 2468 (1984), C.S. Wen et al., Teh. Proc. Conf. Rad. Curing ASIA, p. 478, Tokyo, Oct. (1988), U.S. Patents 4,069,055 and 4,069,056, etc., iodonium salts described in J.V. Crivello et al., Macromolecules, 10 (6) 1307 (1977), Chem. & Eng. News, Nov. 28, p. 31 (1988), European Patents 104,143, 339,049 and 410,201, JP-A-2-150848, JP-A-2-296514, etc., sulfonium salts described in

J.V. Crivello et al., Polymer J., 17, 73 (1985), J.V. Crivello et al., J. Org. Chem., 43, 3055 (1978), W.R. Watt et al., J. Polymer Sci., Polymer Chem. Ed., 22, 1789 (1984), J.V. Crivello et al., Polymer Bull., 14, 279 (1985), J.V. Crivello et al., Macromolecules, 14 (5), 1141 (1981), J.V. Crivello et al., J. Polymer Sci., Polymer Chem. Ed., 17, 2877 (1979), European Patents 370,693, 161,811, 410,201, 339,049, 233,567, 297,443 and 297,442, U.S. Patents 4,933,377, 3,902,114, 4,760,013, 4,734,444 and 2,833,827, German Patent 2,904,626, 3,604,580 and 3,604,581, etc., selenonium salts described in J.V. Crivello et al., Macromolecules, 10 (6), 1307 (1977), J.V. Crivello et al., J. Polymer Sci., Polymer Chem. Ed., 17, 1047 (1979), etc., and arsonium salts described in C.S. Wen et al., Teh. Proc. Conf. Rad. Curing ASIA, p. 478, Tokyo, Oct. (1988), etc.; organic halogen compounds described in U.S. Patent 3,905,815, JP-B-46-4605 (the term "JP-B" as used herein means an "examined Japanese patent publication"), JP-A-48-36281, JP-A-55-32070, JP-A-60-239736, JP-A-61-169835, JP-A-61-169837, JP-A-62-58241, JP-A-62-212401, JP-A-63-70243, JP-A-63-298339, etc.; organic metals/organic halides described in K. Meier et al., J. Rad. Curing, 13 (4), 26 (1986), T.P. Gill et al., Inorg. Chem., 19, 3007 (1980), D. Astruc, Acc. Chem. Res., 19 (12), 377 (1986), JP-A-2-161445, etc.; photo-acid generators having an O-nitrobenzyl type

protective group described in S. Hayase et al., J. Polymer Sci., 25, 753 (1987), E. Reichmanis et al., J. Polymer Sci., Polymer Chem. Ed., 23, 1 (1985), Q.Q. Zhu et al., J. Photochem., 36, 85, 39, 317 (1987), B. Amit et al., Tetrahedron Lett., (24) 2205 (1973), D.H.R. Barton et al., J. Chem. Soc., 3571 (1965), P.M. Collins et al., J. Chem. Soc., Perkin I, 1695 (1975), M. Rudinstein et al., Tetrahedron Lett., (17), 1445 (1975), J.W. Walker et al., J. Am. Chem. Soc., 110, 7170 (1988), S.C. Busman et al., J. Imaging Technol., 11 (4), 191 (1985), H.M. Houlihan et al., Macromolecules, 21, 2001 (1988), P.M. Collins et al., J. Chem. Soc., Chem. Commun., 532 (1972), S. Hayase et al., Macromolecules, 18, 1799 (1985), E. Reichmanis et al., J. Electrochem. Soc., Solid State Sci. Technol., 130 (6), F.M. Houlihan et al., Macromolecules, 21, 2001 (1988), European Patents 0,290,750, 046,083, 156,535, 271,851 and 0,388,343, U.S. Patents 3,901,710 and 4,181,531, JP-A-60-198538, JP-A-53-133022, etc.; compounds which are photodegraded to generate a sulfonic acid, represented by iminosulfonate, described in M. TUNOOKA et al., Polymer Preprints Japan, 35 (8), G. Berner et al., J. Rad. Curing, 13 (4), W.J. Mijs et al., Coating Technol., 55 (697), 45 (1983), Akzo, H. Adachi et al., Polymer Preprints, Japan, 37 (3), European Patents 0,199,672, 84,515, 044,115, 618,564 and 0,101,122, U.S. Patents 4,371,605 and 4,431,774, JP-A-64-18143, JP-A-2-

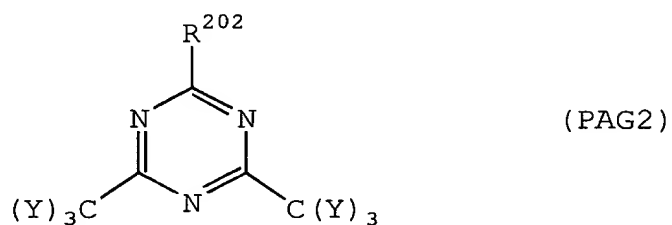
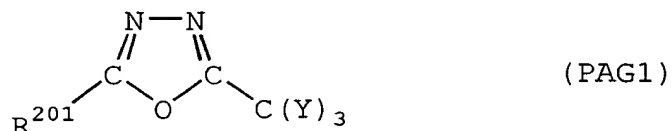
245756, JP-A-3-140109, etc.; and disulfone compounds described in JP-A-61-166544.

In addition, compounds in which the above-described group or compound capable of generating an acid upon irradiation with actinic rays or radiation is introduced into the main chain or side chain of a polymer may also be used and examples thereof include the compounds described in M.E. Woodhouse et al., J. Am. Chem. Soc., 104, 5586 (1982), S.P. Pappas et al., J. Imaging Sci., 30 (5), 218 (1986), S. Kondo et al., Makromol. Chem., Rapid Commun., 9, 625 (1988), Y. Yamada et al., Makromol. Chem., 152, 153, 163 (1972), J.V. Crivello et al., J. Polymer Sci., Polymer Chem. Ed., 17, 3845 (1979), U.S. Patent 3,849,137, German Patent 3,914,407, JP-A-63-26653, JP-A-55-164824, JP-A-62-69263, JP-A-63-146038, JP-A-63-163452, JP-A-62-153853, JP-A-63-146029, etc.

Furthermore, the compounds capable of generating an acid upon irradiation with light, described in V.N.R. Pillai, Synthesis, (1), 1 (1980), A. Abad et al., Tetrahedron Lett., (47) 4555 (1971), D.H.R. Barton et al., J. Chem. Soc., (C), 329 (1970), U.S. Patent 3,779,778, European Patent 126,712, etc. may also be used.

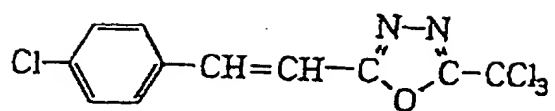
Among these compounds capable of decomposing upon irradiation with actinic rays or radiation to generate an acid, particularly effective compounds are described below.

(1) Oxazole derivative represented by the following formula (PAG1) and S-triazine derivative represented by formula (PAG2), which are each substituted by trihalomethyl group:

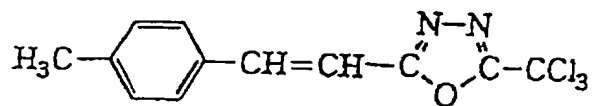


wherein R^{201} represents a substituted or unsubstituted aryl group or a substituted or unsubstituted alkenyl group, R^{202} represents a substituted or unsubstituted aryl group, a substituted or unsubstituted alkenyl group, a substituted or unsubstituted alkyl group or $-\text{C}(\text{Y})_3$, and Y represents a chlorine atom or a bromine atom.

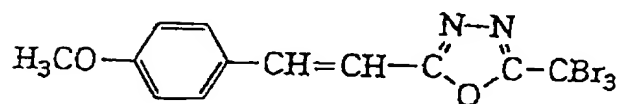
Specific examples thereof include the following compounds, however, the present invention is not limited thereto.



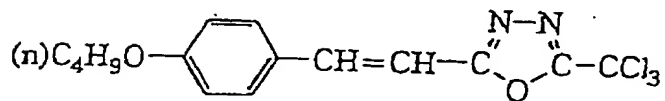
(PAG1-1)



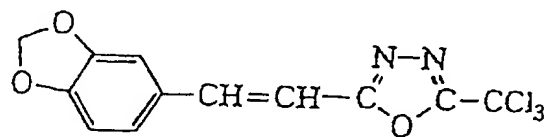
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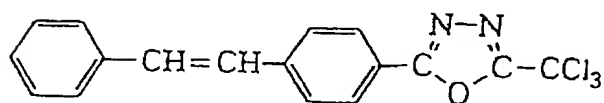
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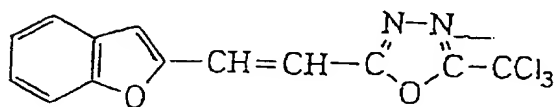
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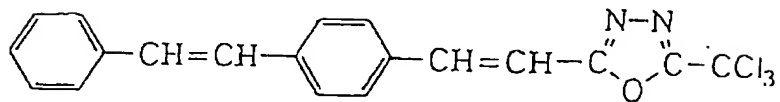
(PAG1-5)



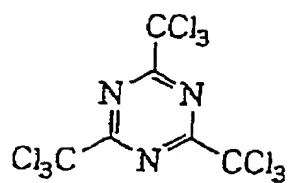
(PAG1-6)



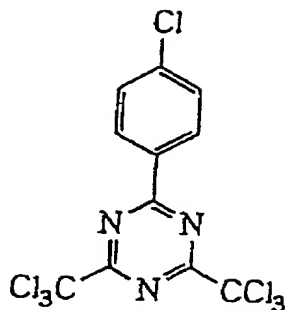
(PAG1-7)



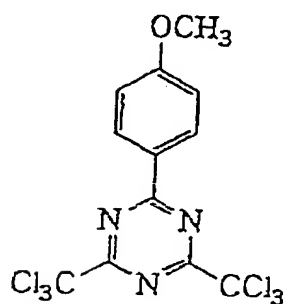
(PAG1-8)



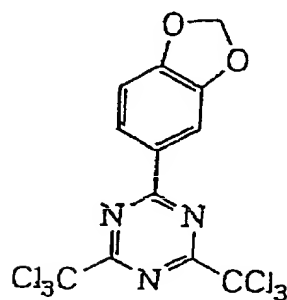
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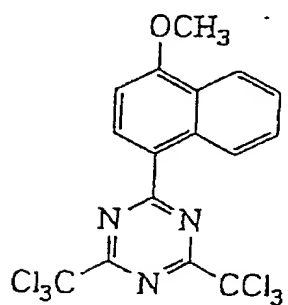
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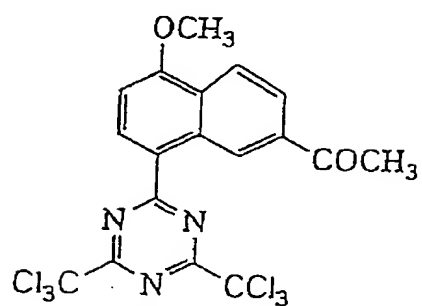
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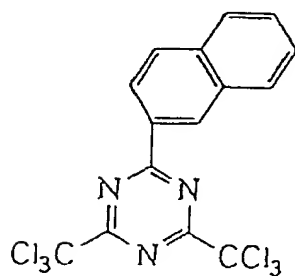
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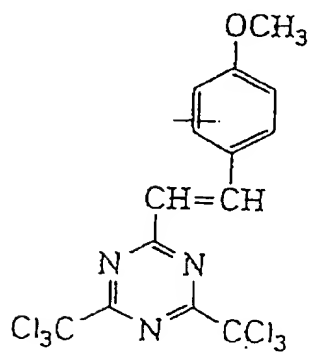
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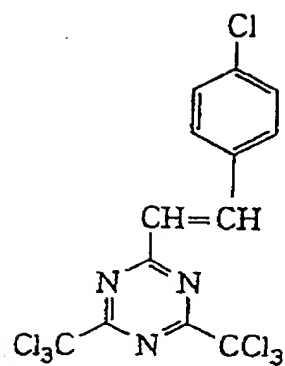
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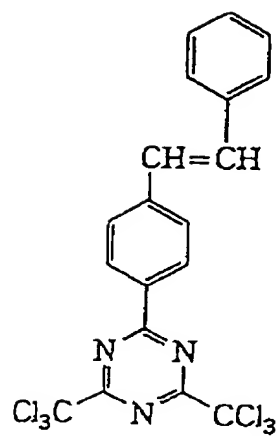
(PAG2-7)



(PAG2-8)

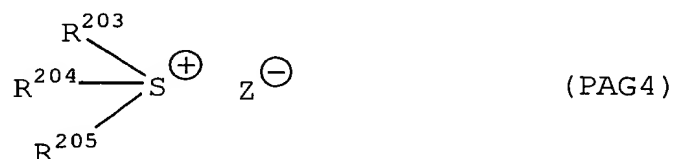


(PAG2-9)



(PAG2-10)

(2) Iodonium salt represented by the following formula (PAG3) and sulfonium salt represented by formula (PAG4):



wherein Ar^1 and Ar^2 each independently represents a substituted or unsubstituted aryl group. The substituent is preferably an alkyl group, a haloalkyl group, a cycloalkyl group, an aryl group, an alkoxy group, a nitro group, a carboxyl group, an alkoxycarbonyl group, a hydroxy group, a mercapto group or a halogen atom.

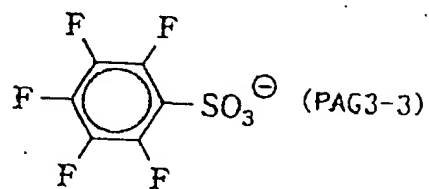
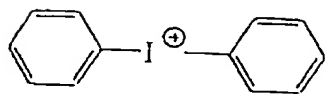
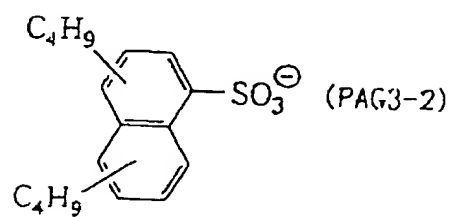
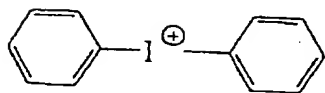
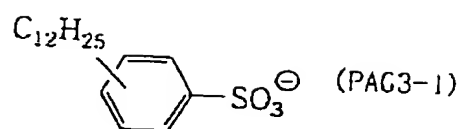
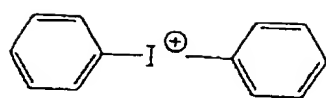
R^{203} , R^{204} and R^{205} each independently represents a substituted or unsubstituted alkyl group or a substituted or unsubstituted aryl group, and preferably an aryl group having from 6 to 14 carbon atoms, an alkyl group having from 1 to 8 carbon atoms or a substituted derivative thereof. The substituent of the aryl group is preferably an alkoxy group having from 1 to 8 carbon atoms, an alkyl group having from 1 to 8 carbon atoms, a cycloalkyl group, a nitro group, a carboxyl group, a mercapto group, a

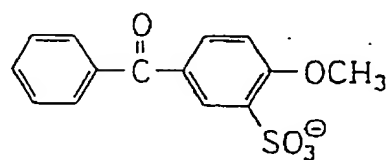
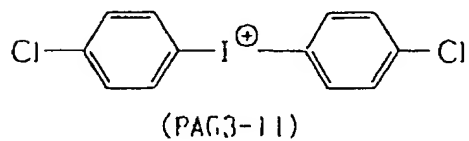
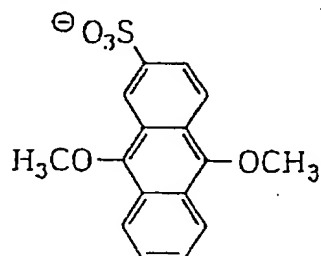
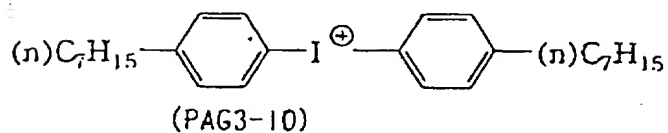
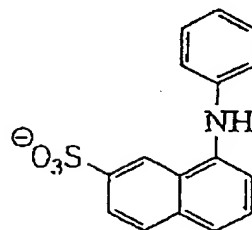
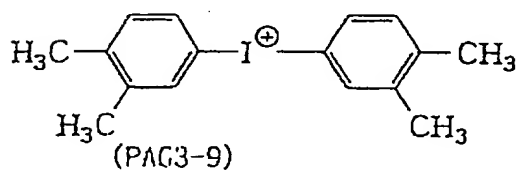
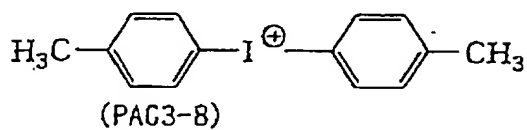
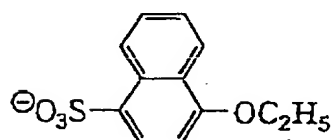
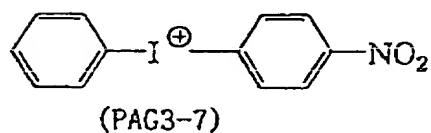
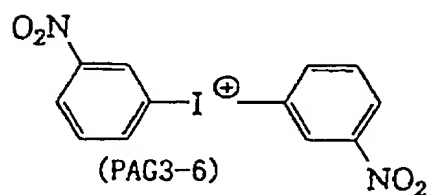
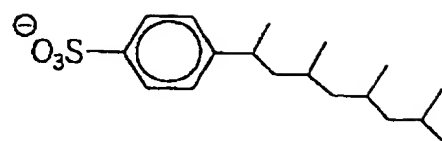
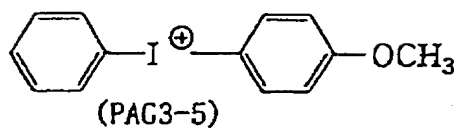
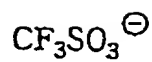
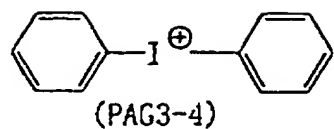
hydroxy group or a halogen atom, and the substituent of the alkyl group is preferably an alkoxy group having from 1 to 8 carbon atoms, a carboxyl group or an alkoxycarbonyl group.

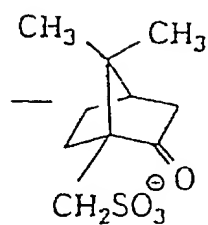
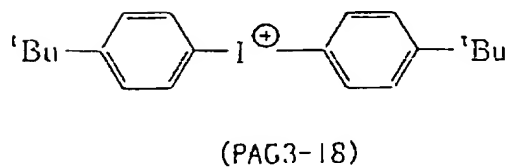
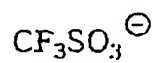
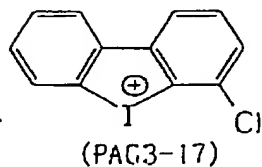
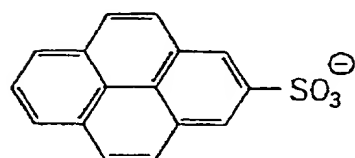
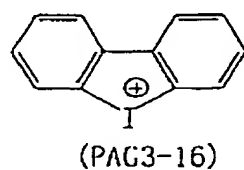
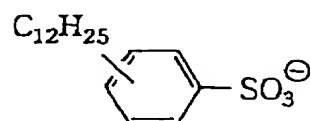
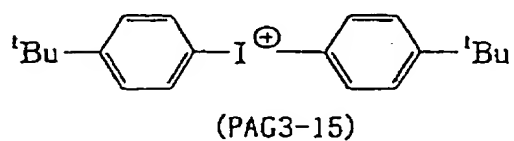
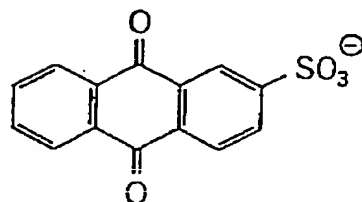
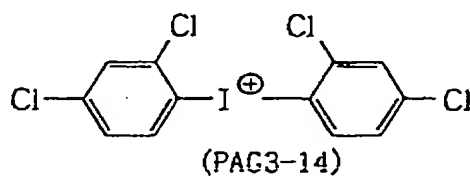
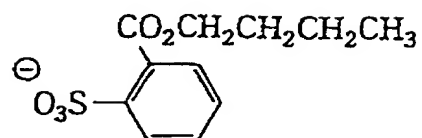
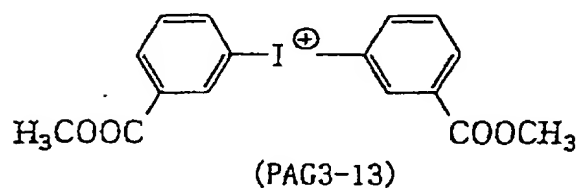
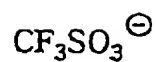
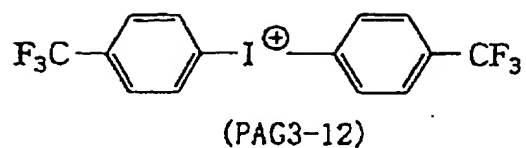
Z^- represents an anion and specific examples thereof include alkyl sulfonate anion, cycloalkyl sulfonate anion, perfluoroalkyl sulfonate anion and aryl sulfonate anion (e.g., benzenesulfonate anion, naphthalene sulfonate anion and anthracene sulfonate, each of which may have a substituent).

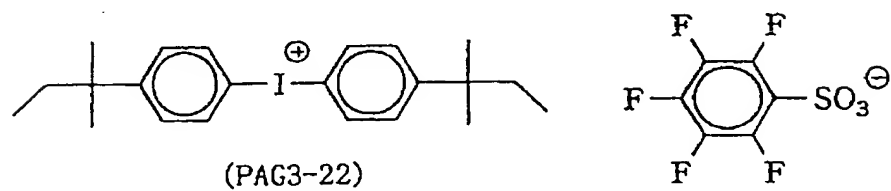
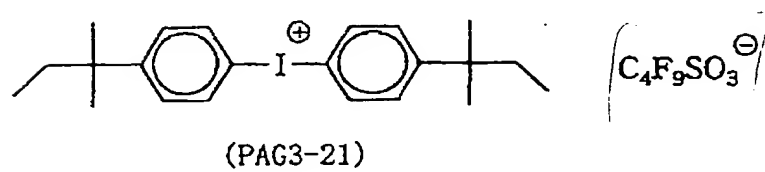
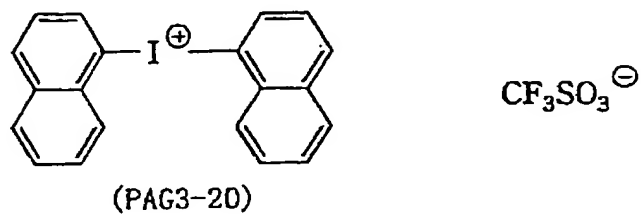
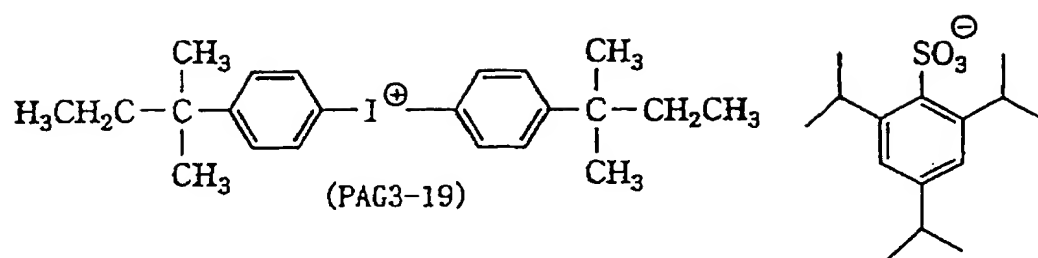
Two of R^{203} , R^{204} and R^{205} , or Ar^1 and Ar^2 may be combined through a single bond or a substituent.

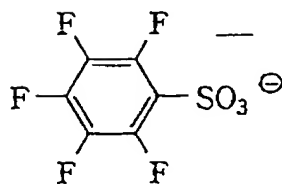
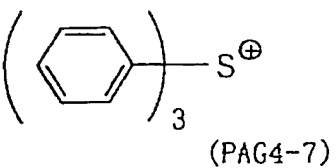
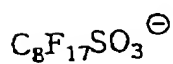
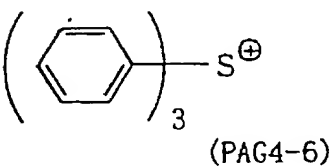
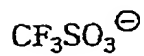
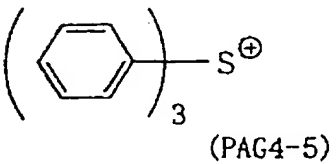
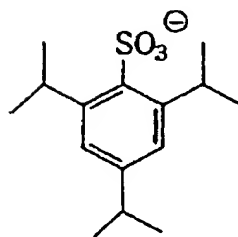
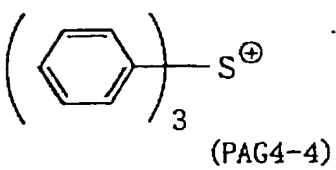
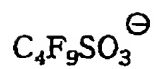
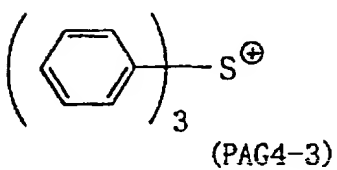
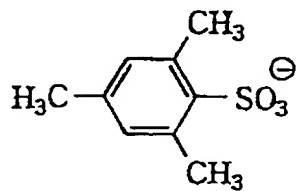
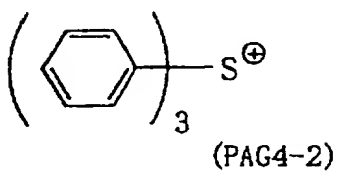
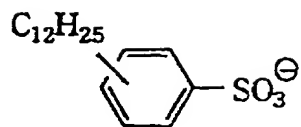
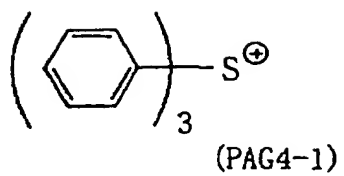
Specific examples thereof include the following compounds, however, the present invention is not limited thereto.

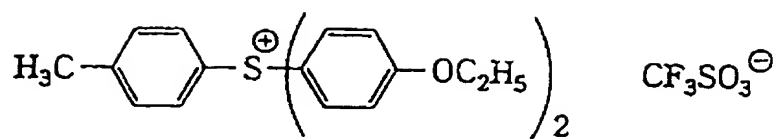




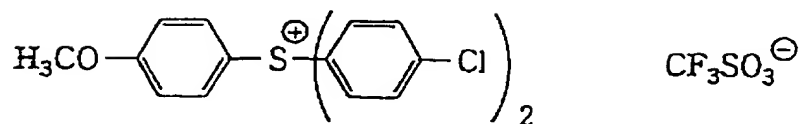




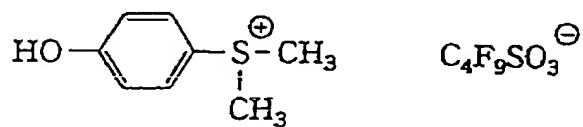




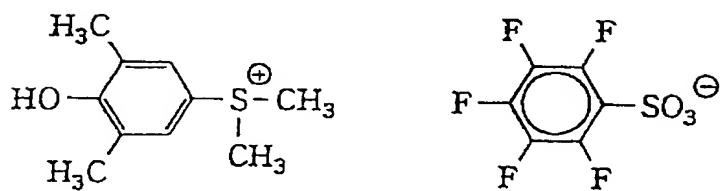
(PAG4-8)



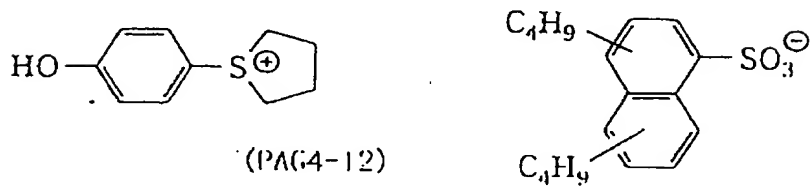
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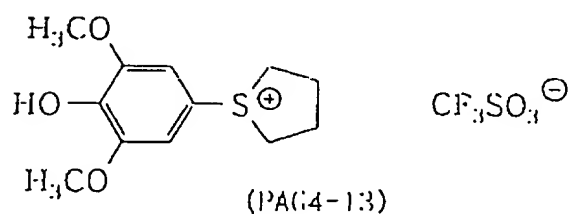
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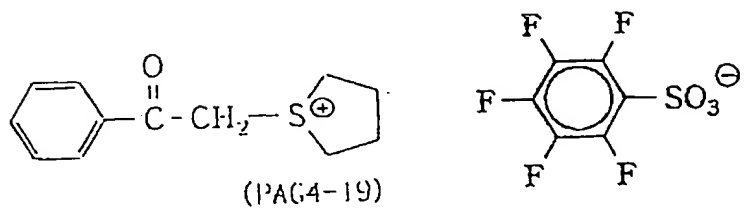
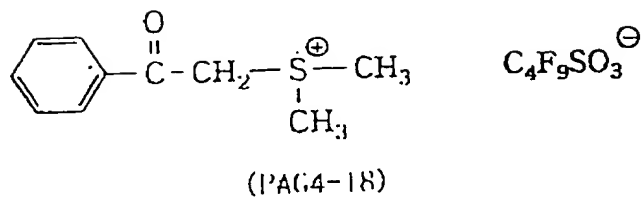
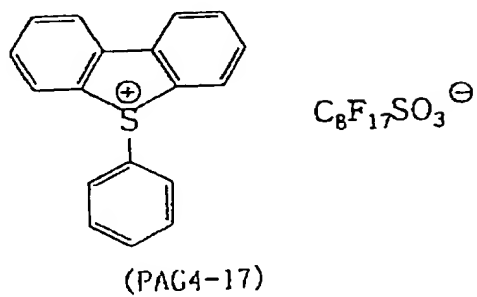
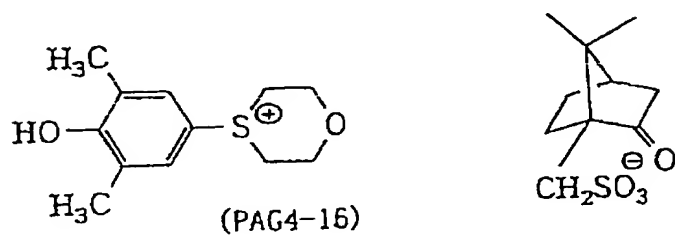
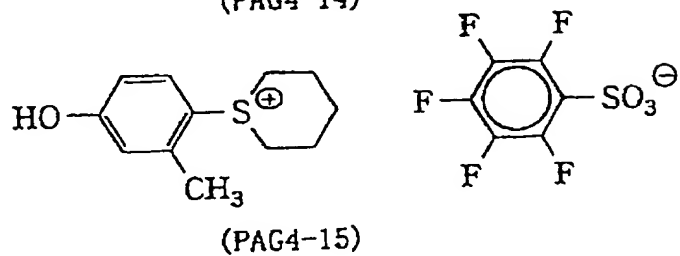
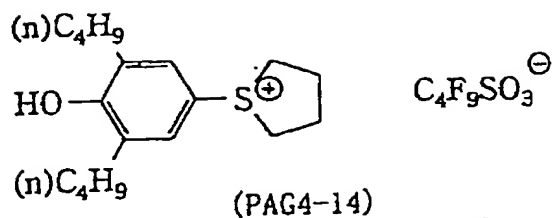
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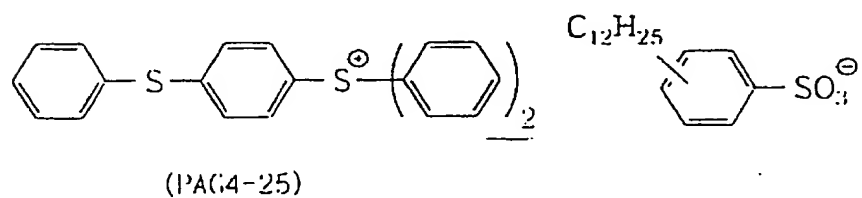
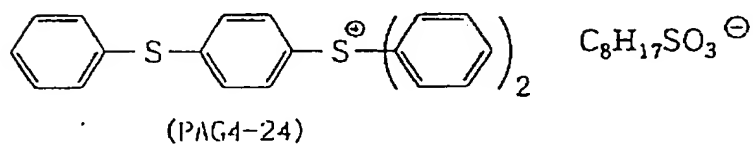
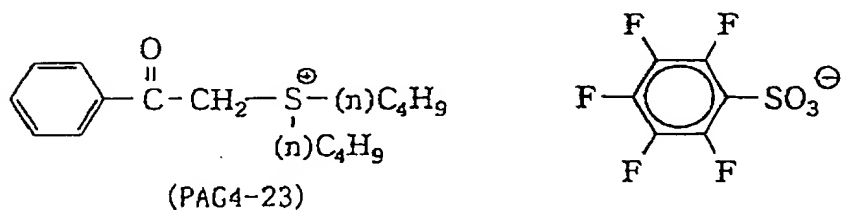
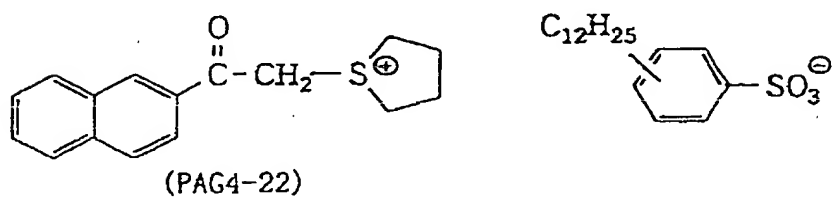
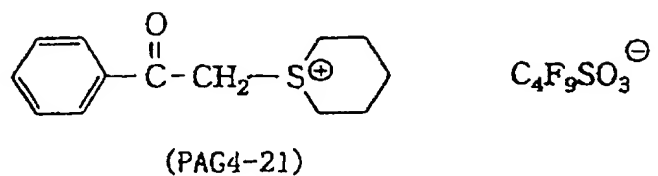
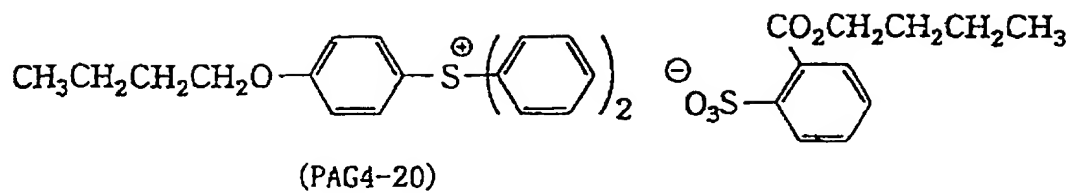


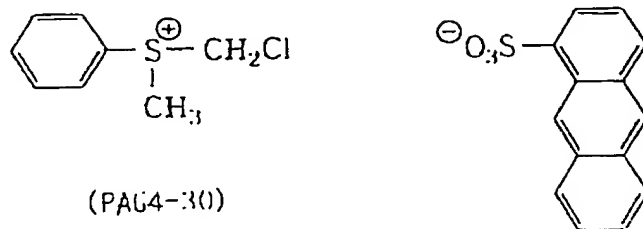
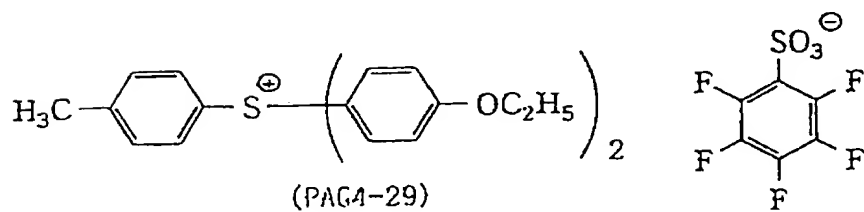
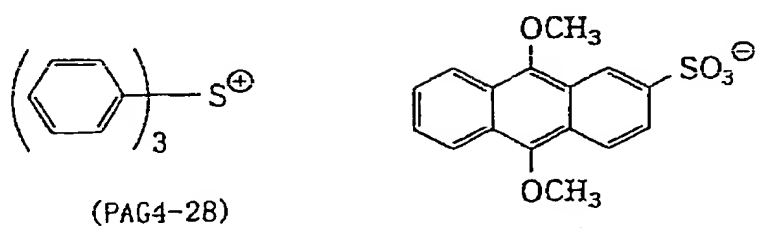
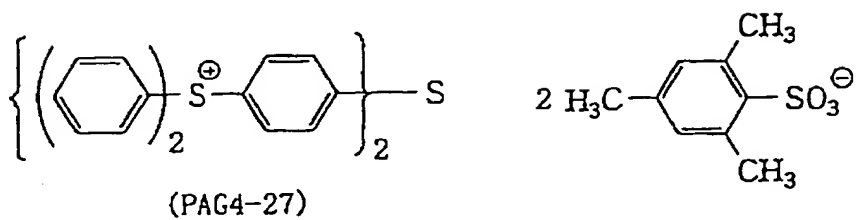
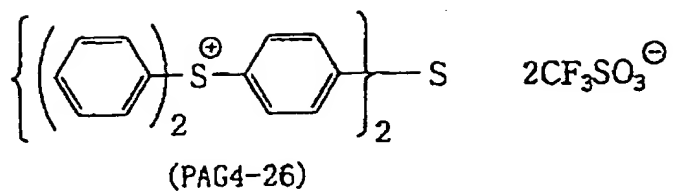
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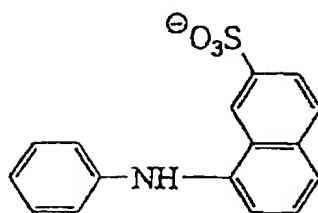
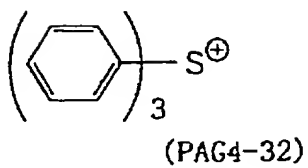
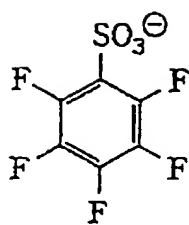
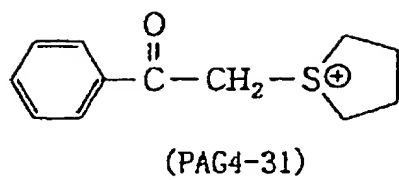


(PAG4-13)



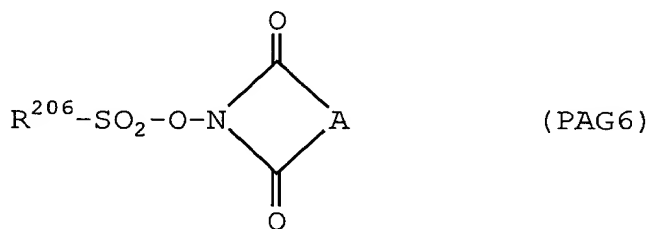






The above-mentioned onium salts represented by formulae (PAG3) and (PAG4) are known and can be synthesized by the method described, for example, in J.W. Knapczyk et al., J. Am. Chem. Soc., 91, 145 (1969), A.L. Maycok et al., J. Org. Chem., 35, 2532 (1970), E. Goethas et al., Bull. Soc. Chem. Belg., 73, 546 (1964), H.M. Leicester, J. Ame. Chem. Soc., 51, 3587 (1929), J.V. Crivello et al., J. Polym. Chem. Ed., 18, 2677 (1980), U.S. Patents 2,807,648 and 4,247,473, JP-A-53-101331, etc.

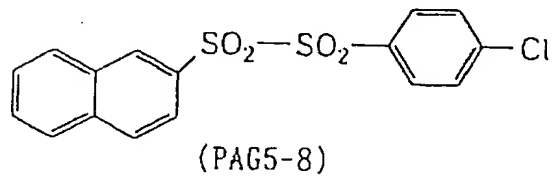
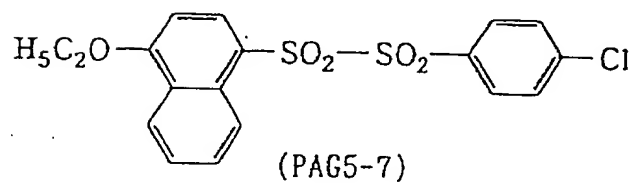
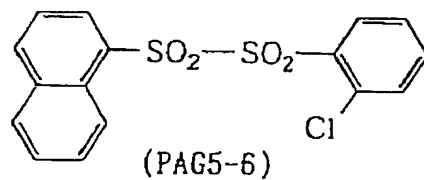
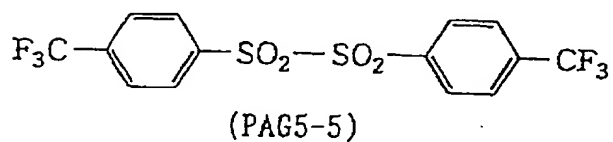
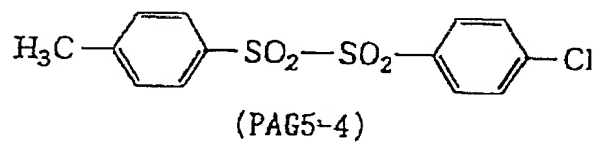
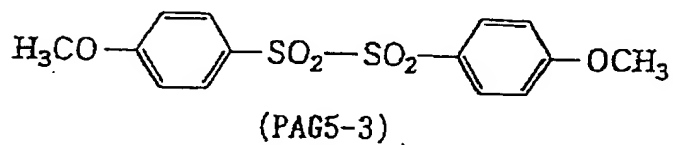
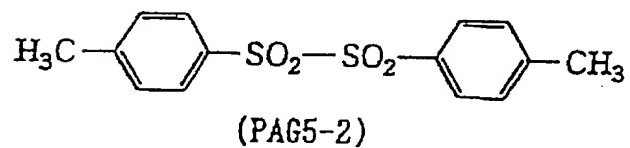
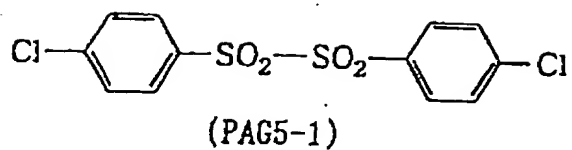
(3) Disulfone derivative represented by the following formula (PAG5) and iminosulfonate derivative represented by formula (PAG6):

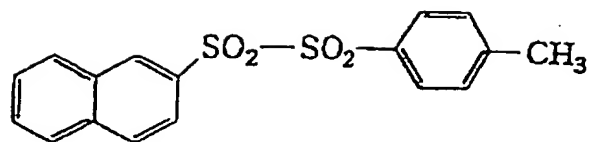


wherein Ar^3 and Ar^4 each independently represents a substituted or unsubstituted aryl group, R^{206} represents a substituted or unsubstituted alkyl group or a substituted or unsubstituted aryl group, and A represents a substituted or unsubstituted alkylene group, a substituted or

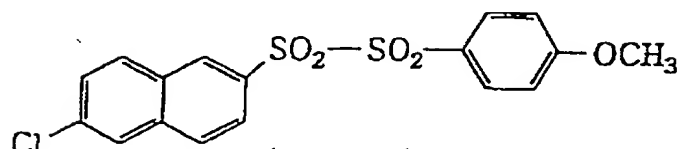
unsubstituted alkenylene group or a substituted or unsubstituted arylene group.

Specific examples thereof include the following compounds, however, the present invention is not limited thereto.

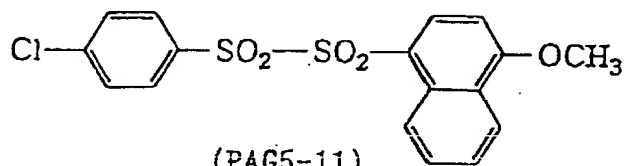




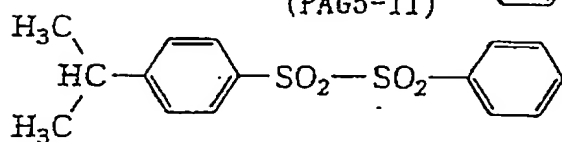
(PAG5-9)



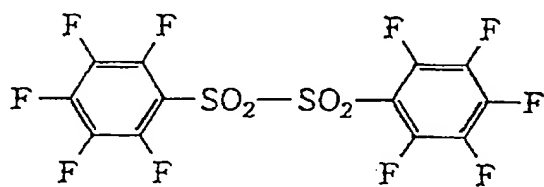
(PAG5-10)



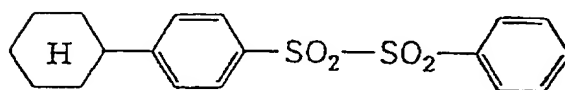
(PAG5-11)



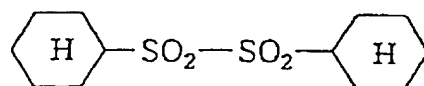
(PAG5-12)



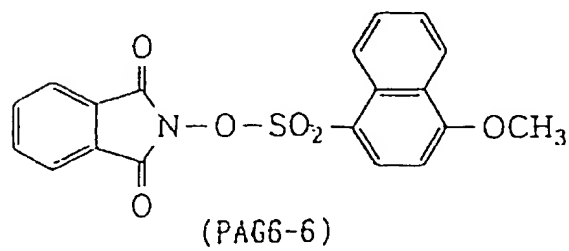
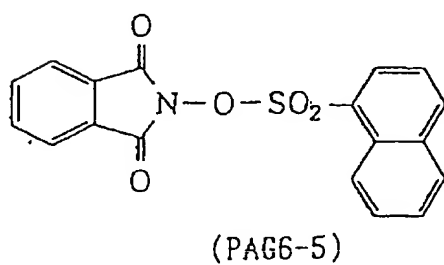
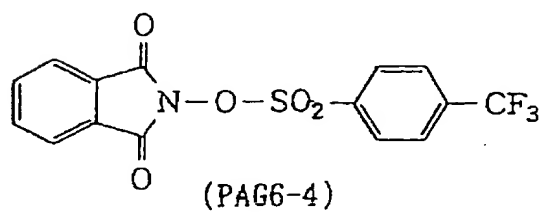
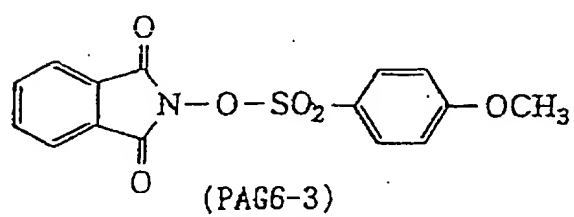
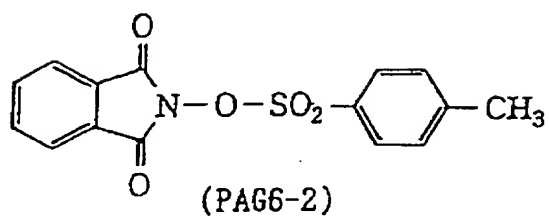
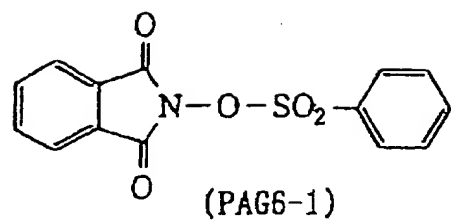
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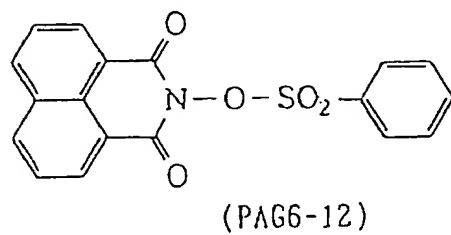
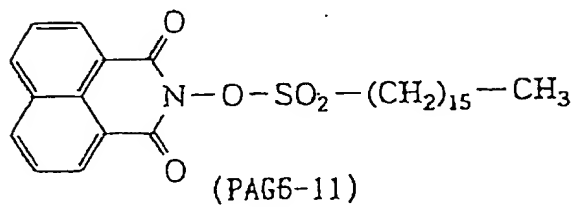
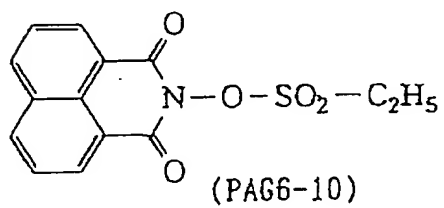
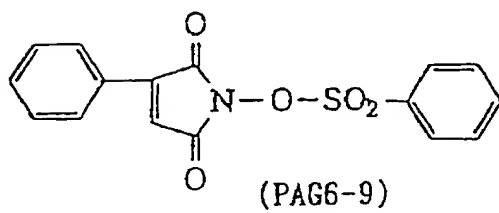
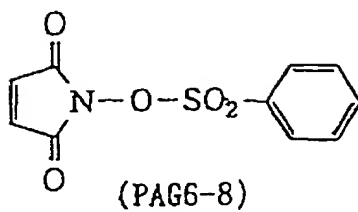
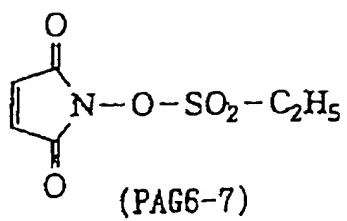


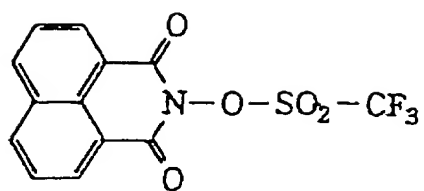
(PAG5-14)



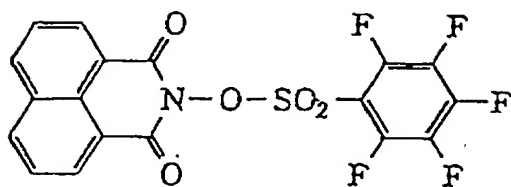
(PAG5-15)



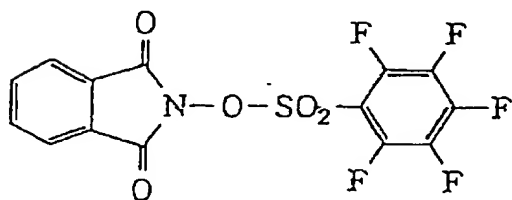




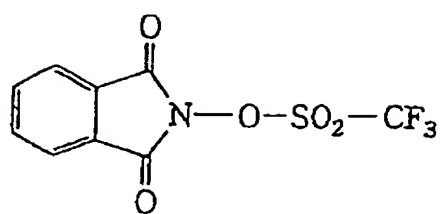
(PAG6-13)



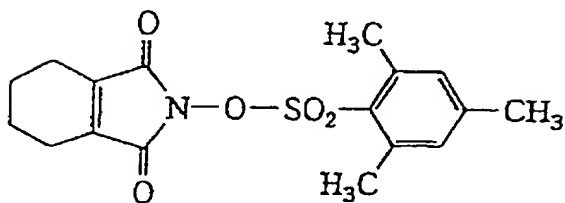
(PAG6-14)



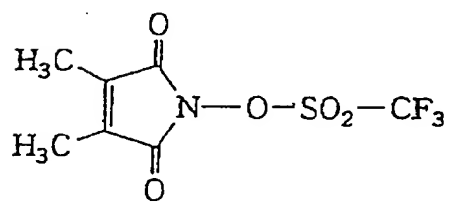
(PAG6-15)



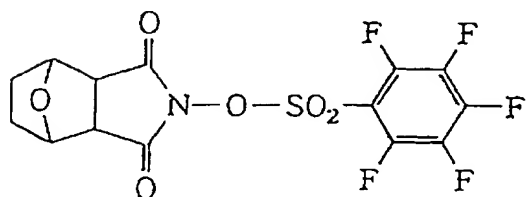
(PAG6-16)



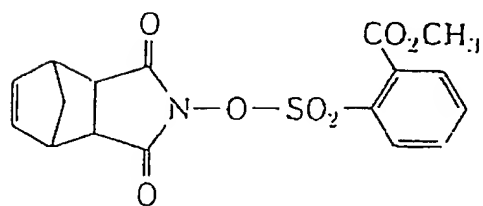
(PAG6-17)



(PAG6-18)



(PAG6-19)



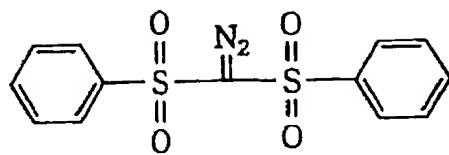
(PAG6-20)

(4) Diazodisulfone derivative compound represented by the following formula (PAG7)

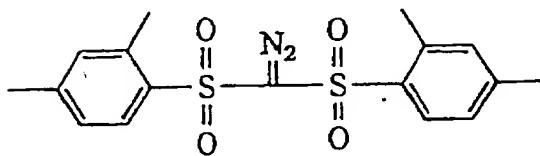


wherein R represents a linear, branched or cyclic alkyl group or an aryl group which may be substituted.

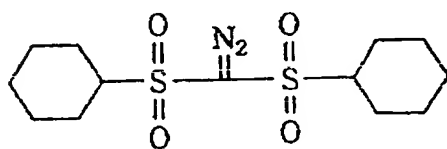
Specific examples thereof include the following compounds, however, the present invention is not limited thereto.



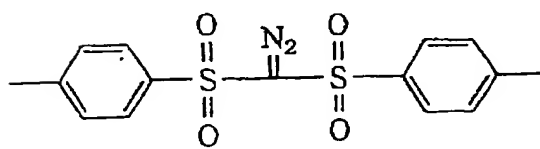
(PAG7-1)



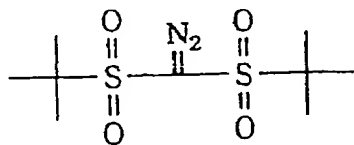
(PAG7-2)



(PAG7-3)



(PAG7-4)



(PAG7-5)

The amount added of the compound (B) capable of generating an acid upon irradiation with actinic rays or radiation, which is used in the present invention, is from 0.1 to 20% by weight, preferably from 0.5 to 10% by weight, more preferably from 1 to 7% by weight, based on the entire solid content of the composition of the present invention. These compounds may be used individually or as a mixture of a plurality of the compounds.

[3] Surfactant (C) of the present invention (Fluorine-containing and/or silicon-containing surfactant)

The positive photoresist composition of the present invention contains a fluorine-containing and/or silicon-containing surfactant (C). More specifically, the positive photoresist composition of the present invention contains any one of a fluorine-containing surfactant, a silicon-containing surfactant and a surfactant containing both a fluorine atom and a silicon atom, or contains two or more thereof. By the addition of this fluorine-containing and/or silicon-containing surfactant, the development defect is prevented and the coatability is improved.

Examples of these surfactants include surfactants described in JP-A-62-36663, JP-A-61-226746, JP-A-61-226745, JP-A-62-170950, JP-A-63-34540, JP-A-7-230165, JP-A-8-62834, JP-A-9-54432, JP-A-9-5988 and U.S. Patents 5,405,720,

5,360,692, 5,529,881, 5,296,330, 5,436,098, 5,576,143, 5,296,143, 5,294,511 and 5,824,451. The following commercially available surfactants each may also be used as it is.

Examples of the commercially available surfactant which can be used include fluorine-containing surfactants and silicon-containing surfactants, such as Eftop EF301, EF303 and EF352 (produced by Shin-Akita Kasei K.K.), Florad FC430 and 431 (produced by Sumitomo 3M Inc.), Megafac F171, F173, F176, F189 and R08 (produced by Dainippon Ink & Chemicals, Inc.), Asahi Guard AG710, Surflon S-382, SC101, 102, 103, 104, 105 and 106 (produced by Asahi Glass Co., Ltd.), and Troysol S-366 (produced by Troy Chemical). In addition, polysiloxane polymer KP-341 (produced by Shin-Etsu Chemical Co., Ltd.) may also be used as a silicon-containing surfactant.

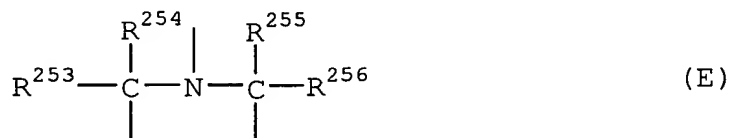
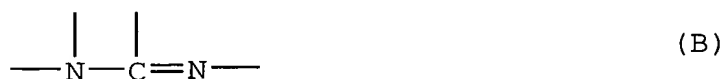
The amount of the surfactant blended is usually from 0.001 to 2% by weight, preferably from 0.01 to 1% by weight, based on the solid content in the composition of the present invention. These surfactants may be added individually or in combination of two or more thereof.

[4] Acid diffusion inhibitor (D) of the present invention

The composition of the present invention preferably contains an acid diffusion inhibitor for the purpose of

preventing fluctuation in performance (e.g., T-top shape formation of pattern, fluctuation in sensitivity, fluctuation in line width of pattern) with the passage of time after the irradiation with actinic rays or radiation until the heat-treatment, fluctuation due to aging after the coating, or excess diffusion of acid (deterioration of resolution) at the time of heat-treatment after the irradiation with actinic rays or radiation. The acid diffusion inhibitor is an organic basic compound, for example, an organic basic compound containing a basic nitrogen, and a compound where the conjugate acid has a pKa value of 4 or more is preferably used.

Specific examples thereof include a compound having the following structures (A) to (E):



wherein R^{250} , R^{251} and R^{252} , which may be the same or different, each represents a hydrogen atom, an alkyl group having from 1 to 6 carbon atoms, an aminoalkyl group having from 1 to 6 carbon atoms, a hydroxyalkyl group having from 1 to 6 carbon atoms or a substituted or unsubstituted aryl group having from 6 to 20 carbon atoms, provided that R^{251} and R^{252} may combine with each other to form a ring; and

R^{253} , R^{254} , R^{255} and R^{256} , which may be the same or different, each represents an alkyl group having from 1 to 6 carbon atoms.

The compound is more preferably a nitrogen-containing basic compound having two or more nitrogen atoms different in the chemical environment within one molecule, still more preferably a compound having both a substituted or unsubstituted amino group and a ring structure containing a nitrogen atom, or a compound having an alkylamino group.

Specific preferred examples thereof include a substituted or unsubstituted guanidine, a substituted or unsubstituted aminopyridine, a substituted or unsubstituted aminoalkylpyridine, a substituted or unsubstituted aminopyrrolidine, a substituted or unsubstituted indazole, an imidazole, a substituted or unsubstituted pyrazole, a substituted or unsubstituted pyrazine, an substituted or unsubstituted pyrimidine, a substituted or unsubstituted purine, a substituted or unsubstituted imidazoline, a

substituted or unsubstituted pyrazoline, a substituted or unsubstituted piperazine, a substituted or unsubstituted aminomorpholine and a substituted or unsubstituted aminoalkylmorpholine. The substituent is preferably an amino group, an aminoalkyl group, an alkylamino group, an aminoaryl group, an arylamino group, an alkyl group, an alkoxy group, an acyl group, an acyloxy group, an aryl group, an aryloxy group, a nitro group, a hydroxyl group or a cyano group.

More preferred compounds are guanidine, 1,1-dimethylguanidine, 1,1,3,3-tetramethylguanidine, imidazole, 2-methylimidazole, 4-methylimidazole, N-methylimidazole, 2-phenylimidazole, 4,5-diphenylimidazole, 2,4,5-triphenylimidazole, 2-aminopyridine, 3-aminopyridine, 4-aminopyridine, 2-dimethylaminopyridine, 4-dimethylaminopyridine, 2-diethylaminopyridine, 2-(aminomethyl)pyridine, 2-amino-3-methylpyridine, 2-amino-4-methylpyridine, 2-amino-5-methylpyridine, 2-amino-6-methylpyridine, 3-aminoethylpyridine, 4-aminoethylpyridine, 3-aminopyrrolidine, piperazine, N-(2-aminoethyl)piperazine, N-(2-aminoethyl)piperidine, 4-amino-2,2,6,6-tetramethylpiperidine, 4-piperidinopiperidine, 2-iminopiperidine, 1-(2-aminoethyl)pyrrolidine, pyrazole, 3-amino-5-methylpyrazole, 5-amino-3-methyl-1-p-tolylpyrazole, pyrazine, 2-(aminomethyl)-5-methylpyrazine, pyrimidine,

2,4-diaminopyrimidine, 4,6-dihydroxypyrimidine, 2-pyrazoline, 3-pyrazoline, N-aminomorpholine and N-(2-aminoethyl)morpholine. However, the present invention is not limited thereto.

These nitrogen-containing basic compounds are used individually or in combination of two or more thereof.

The ratio between the acid generator and the organic basic compound used in the composition is preferably 2.5 to 300 $\{(\text{acid generator})/(\text{organic basic compound}) \text{ (by mol)}\}$. If this molar ratio is less than 2.5, low sensitivity results and the resolution may decrease in some cases, whereas if it exceeds 300, the thickening of the pattern increases in aging after the exposure until the heat-treatment and the resolution sometimes decreases. The $(\text{acid generator})/(\text{organic basic compound}) \text{ (by mol)}$ is preferably from 5.0 to 200, more preferably from 7.0 to 150.

[5] Other components used in the composition of the present invention

(1) Solvents

The composition of the present invention is dissolved in a solvent which can dissolve the above-described respective components, and then coated on a substrate. The solvent used here is preferably ethylene dichloride, cyclohexanone, cyclopentanone, 2-heptanone, γ -butyrolactone,

methyl ethyl ketone, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, 2-methoxyethyl acetate, ethylene glycol monoethyl ether acetate, propylene glycol monomethyl ether, propylene glycol monoethyl ether, propylene glycol monomethyl ether acetate, toluene, ethyl acetate, methyl lactate, ethyl lactate, methyl methoxypropionate, ethyl ethoxypropionate, methyl pyruvate, ethyl pyruvate, propyl pyruvate, N,N-dimethylformamide, dimethyl sulfoxide, N-methylpyrrolidone or tetrahydrofuran. These solvents are used individually or in combination.

For forming a pattern on a resist film, for example, in the production of a precision integrated circuit device, the positive photoresist composition of the present invention is coated on a substrate (e.g., transparent substrate such as silicon/silicon dioxide coating, glass substrate and ITO substrate), irradiated with actinic rays or radiation using a drawing apparatus, heated, developed, rinsed and dried, whereby a good resist pattern can be formed.

The developer which can be used for the positive resist composition of the present invention is an aqueous solution of an alkali such as inorganic alkalis (e.g., sodium hydroxide, potassium hydroxide, sodium carbonate, sodium silicate, sodium metasilicate, aqueous ammonia), primary amines (e.g., ethylamine, n-propylamine), secondary

amines (e.g., diethylamine, di-n-butylamine), tertiary amines (e.g., triethylamine, methyldiethylamine), alcohol amines (e.g., dimethylethanolamine, triethanolamine), quaternary ammonium salts (e.g., tetramethylammonium hydroxide, tetraethylammonium hydroxide, choline) or cyclic amines (e.g., pyrrole, piperidine). This aqueous alkali solution may be used after adding thereto an appropriate amount of an alcohol (e.g., isopropyl alcohol) or surfactant (e.g., nonionic surfactant).

Among these developers, preferred are quaternary ammonium salts, more preferred are tetramethylammonium hydroxide and choline.

[Example]

The present invention is described in greater detail in the following examples, however, the present invention should not be construed as being limited thereto.

[SYNTHESIS EXAMPLE 1]

A 150-ml 1,1,2-trichloro-trifluoroethylene solution containing 9.4 g (0.10 mol) of norbornene and 19.4 g (0.10 mol) of tert-butyl norbornene-2-carbonate was charged into a 1 L-volume autoclave and a pressure was applied to 200 psi in a nitrogen atmosphere. Furthermore, 20 g (0.20 mol) of tetrafluoroethylene was injected and heated at 50°C while stirring. To the reaction solution, a 15-ml 1,1,2-

trichloro-trifluoroethylene solution containing 1.2 g of di(4-tert-butylcyclohexyl)peroxydicarbonate was injected over 20 minutes and the solution was continuously stirred for 20 hours. After the completion of reaction, the reaction solution was charged into 2 L of methanol while vigorously stirring to precipitate a white resin. The precipitated resin was separated by filtration and dried in a vacuum to obtain 23.5 g of Resin (1) of the present invention.

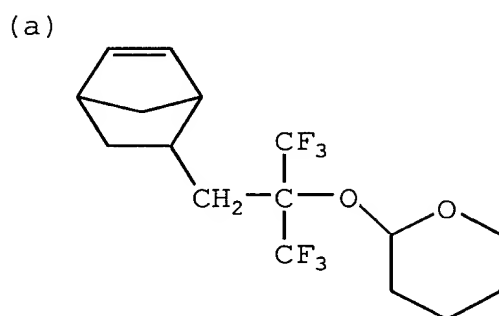
By the GPC measurement, the molecular weight of Resin (1) was 6,200 as a weight average (Mw). Also, the composition of Resin (1) was examined by the C^{13} -NMR measurement and found to be Structure (F-1)/norbornene/(B-16) = 45/30/25 by mol.

[SYNTHESIS EXAMPLE 2]

14.3 g (0.04 mol) of Monomer (a) shown below, 3.9 g (0.04 mol) of maleic anhydride and 2.6 g (0.02 mol) of tert-butyl acrylate were dissolved in 100 ml of MEK and heated at 70°C in a nitrogen stream. Thereto, 0.2 g of V-601 (produced by Wako Pure Chemical Industries, Ltd.) was added as a polymerization initiator and the solution was stirred for 3 hours. Then, 0.2 g of V-601 was added and the solution was continuously stirred for 4 hours. Thereafter, the reaction solution was charged into 1 L of tert-butyl

methyl ether while vigorously stirring to precipitate a white resin. The precipitated resin was separated by filtration and dried in a vacuum to obtain 12.1 g of Resin (2) of the present invention.

By the GPC measurement, the molecular weight of Resin (2) was 8,900 as a weight average (Mw). Also, the composition of Resin (2) was examined by the C^{13} -NMR measurement and found to be Structure (F-21)/maleic anhydride/(B-4) = 39/38/23 by mol.



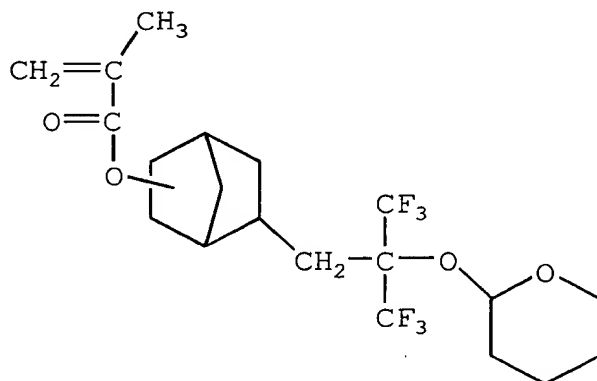
[SYNTHESIS EXAMPLE 3]

6.7 g (0.015 mol) of Monomer (b) shown below, 1.4 g (0.006 mol) of 2-methyl-2-adamantane methacrylate and 1.8 g (0.009 mol) of mevalonic lactone methacrylate were dissolved in 30 ml of 1-methoxy-2-propanol and thereto, 0.1 g of 2,2'-azobis(2,4-dimethylvaleronitrile) (V-65, trade name, produced by Wako Pure Chemical Industries, Ltd.) as a polymerization initiator and a 70-ml 1-methoxy-2-propanol

solution containing 15.6 g (0.035 mol) of Monomer (b), 3.3 g (0.014 mol) of 2-methyl-2-adamantane methacrylate and 4.2 g (0.021 mol) of mevalonic lactone methacrylate were added dropwise over 2 hours at 70°C while stirring in a nitrogen stream. After 2 hours, 0.1 g of the initiator was additionally added and the reaction was further allowed to proceed for 2 hours. Thereafter, the temperature was elevated to 90°C and the stirring was continued for 1 hour. The reaction solution was allowed to cool and then charged into 1 L of ion exchanged water/methanol (1/1) while vigorously stirring to precipitate a white resin. The obtained resin was dried under reduced pressure to obtain 15.8 g of Resin (3) of the present invention.

By the GPC measurement, the molecular weight was 10,200 as a weight average (Mw). Also, the composition of Resin (3) was examined by the C¹³-NMR measurement and found to be Structure (F-30)/(B-7)/(B-11) = 48/21/31 by mol.

(b)



[SYNTHESIS EXAMPLES 4 TO 12]

The resins (A) of the present invention shown in Table 1 below were synthesized in the same manner as above.

TABLE 1

Synthesis of Resin (A) of the Invention

Resin (A)	Composition (structural unit and molar ratio in resin)	Molecular Weight
(4)	(F-1)/(B-20)/(B-23)=45/25/30	5,800
(5)	(F-1)/(F-21)/(B-16)=48/33/19	4,500
(6)	(F-22)/maleic anhydride/(B-8)=42/39/19	8,700
(7)	(F-30)/(F-48)/(B-2)=42/17/41	12,600
(8)	(F-50)/(B-7)/(B-11)=31/35/34	9,200
(9)	(F-55)/maleic anhydride/(B-4)=40/37/23	7,400
(10)	(F-16)/maleic anhydride/(B-8)=43/34/23	6,300
(11)	(F-26)/maleic anhydride/(B-12)=40/33/27	8,900
(12)	(F-31)/(F-42)/(B-8)=44/18/38	11,600

[EXAMPLE 1]

Measurement of Transmittance:

1.36 g of each resin disclosed in the above-described Table 1 and 0.04 g of triphenylsulfonium nonaflate salt were dissolved in 8.5 g of propylene glycol monomethyl ether acetate and thereto, 0.005 g of dicyclohexylmethylamine and as a surfactant, 0.01 g of Megafac R08 (produced by Dainippon Ink & Chemicals Inc.) were added to prepare resist compositions of the present invention.

Each sample solution was filtered through a 0.1- μm Teflon filter, coated on a calcium fluoride disk using a spin coater and dried under heating at 120°C for 5 hours to obtain a resist film having a film thickness of 0.1 μm . The absorption of the coating film was measured by Acton CAMS-507 spectrometer and the transmittance at 157 nm was calculated.

The results are shown in Table 2.

TABLE 2

Resin of the Invention	Transmittance at 157 nm (%)
(1)	58
(2)	52
(3)	53
(4)	56
(5)	63
(6)	51
(7)	68
(8)	52
(9)	51
(10)	55
(11)	50
(12)	49
Comparative Example 1 (commercially available acetal-type resist for KrF)	18

As seen from the results in Table 2, the measured transmittance of the coating film using the composition of the present invention is almost in excess of 50% and this

reveals that the coating film has a sufficiently high transmittance at 157 nm.

[EXAMPLE 2]

Evaluation of Coatability and Development Defect:

The resist compositions of the present invention were prepared by changing the surfactant used in Example 1 to the following W-1 to W-4. The surfactant used is shown in Table 3.

The surfactants used are:

- W1: Megafac F176 (produced by Dainippon Ink & Chemicals Inc.) (containing fluorine)
- W2: Megafac R08 (produced by Dainippon Ink & Chemicals Inc.) (containing fluorine and silicon)
- W3: Polysiloxane polymer KP-341 (produced by Shin-Etsu Chemical Co., Ltd.)
- W4: Polyoxyethylene nonylphenyl ether

Each sample solution was filtered through a 0.1- μm Teflon filter, coated on a silicon wafer treated with hexamethyldisilazane using a spin coater and dried under heating on a vacuum contact-type hot plate at 110°C for 90 seconds to obtain resist films having a film thickness of 0.3 μm . The obtained resist films each was imagewise

exposed using a KrF excimer stepper (FPA-3000EX5) manufactured by Canon, after-heated at 110°C for 90 seconds and then developed with a 0.262N TMAH aqueous solution to form a 0.5- μm L/S pattern.

The development defect and coatability were evaluated as follows.

[Number of development defects]

The resist pattern obtained above was measured on the number of development defects using a machine KLA-2112 manufactured by KLA Tenchol and the obtained primary data value was used as the number of development defects.

[Coatability (in-plane uniformity)]

Each resist solution was coated on a 8-inch silicon wafer and treated in the same manner as in the above-described formation of resist layer to obtain a resist coating film for the measurement of in-plane uniformity. The film thickness of this coating film was measured using Lambda A manufactured by Dainippon Ink & Chemicals Inc. at 36 sites to make a cross at equal intervals along the diameter direction of the wafer.

From the measured values, a standard deviation was determined. When the triple of the standard deviation is less than 50, the rating was ○ and when 50 or more, ×.

The results in the evaluation of performance are shown in Table 3.

TABLE 3

Resin (A) of the Invention	Surfactant Used	Development Defects	Coatability
(1)	W-1	25	○
(2)	W-2	21	○
(3)	W-2	28	○
(4)	W-3	30	○
(5)	W-1	27	○
(6)	W-2	22	○
(7)	W-3	26	○
(8)	W-3	35	○
(9)	W-2	32	○
(10)	W-2	25	○
(11)	W-1	29	○
(12)	W-2	24	○
(1) (Comparative Example 2)	None	2000	×
(1) (Comparative Example 3)	W-4	650	×

As seen from the results in Table 3, the composition of the present invention containing a fluorine and/or silicon-containing surfactant has far excellent coatability and also is greatly reduced in the number of development defects, as compared with Comparative Examples having no the fluorine and/or silicon-containing surfactant.

[EXAMPLE 3]

Evaluation of Image-Forming Property:

Using Resins (1) to (5) of the present invention, resist solutions were prepared in the same manner as in Example 1.

Each sample solution was filtered through a 0.1 μm Teflon filter, coated on a silicon wafer treated with hexamethyldisilazane using a spin coater and dried under heating on a vacuum contact-type hot plate at 110°C for 90 seconds to obtain resist films having a film thickness of 0.1 μm . The obtained resist films each was measured on the dissolution contrast between the exposed area and the unexposed area upon exposure at 157 nm using a 157 nm laser exposure/dissolution behavior analyzer VUVES-4500 (manufactured by Lisotec Japan).

The results are shown in Table 4.

TABLE 4

Resin of the Invention	Dissolution Contrast ($\tan\theta$)
(1)	5.8
(2)	6.5
(3)	6.2
(4)	5.6
(5)	5.9
Comparative Example 4 (commercially available acetal-type resist for KrF)	5.3 ^{*1)}

*1) A value at the exposure by KrF excimer laser (248 nm).

As seen from the results in Table 4, the composition of the present invention provides a dissolution contrast, namely, image-forming property equal to that provided by

the resist practically used for KrF excimer of Comparative Example.

[Advantage of the Invention]

According to the present invention, a positive resist composition exhibiting sufficiently high transmittance and image-forming property even with light at a short wavelength of 157 nm and improved in the problems of coatability and development defect ascribable to fluorine resin can be provided.